SOIL SCIENCE

VOLUME 38

JULY–DECEMBER, 1934

RUTGERS UNIVERSITY
NEW BRUNSWICK, NEW JERSEY
U. S. A.

PUBLISHED BY
THE WILLIAMS & WILKINS COMPANY
BALTIMORE, MARYLAND

SOIL SCIENCE

Editor-in-Chief
JACOB G. LIPMAN

Associate Editor
HERMINIE BROEDEL KITCHEN

ADVISORY STAFF

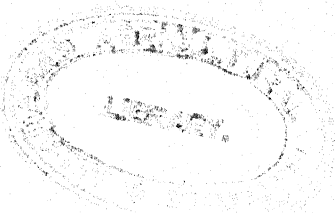
A. W. BLAIR, J. S. JOFFE, L. L. LEE, H. C. MCLEAN, G. T. NIGHTINGALE, A. L. PRINCE, J. W. SHIVE, H. B. SPRAGUE, R. L. STARKEY, AND S. A. WAKSMAN, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

CONSULTING EDITORS

F. J. ALWAY
University of Minnesota, St. Paul, Minn.
K. ASO
Imperial University, Tokyo, Japan
C. BARTHEL
Lantbrukshögskolan, Uppsala, Sweden
P. E. BROWN
Iowa State College of Agriculture, Ames, Iowa
B. C. BURT
Imperial Council of Agricultural Research, New Dehli, India
H. J. CONN
New York State Experiment Station, Geneva, N. Y.
ALBERT DEMOLON
Ministry of Agriculture, Paris, France
E. B. FRED
University of Wisconsin, Madison, Wis.
V. V. GEMMERLING
Agronomitsheskii Institute, Moskovskii Universitat, Moscow, U. S. S. R.
J. E. GREAVES
Utah Agricultural College, Logan, Utah
ACH. GREGOIRE
Agricultural Experiment Station, Gembloux, Belgium
B. L. HARTWELL
26 Rowe St., Auburndale, Mass.
D. J. HISSINK
Soil Science Institute, Groningen, Holland
O. LEMMERMANN
Institut für Agrikulturchemie u. Bakteriologie der Landwirtschaftlichen Hochschule, Berlin-Dahlem, Germany
C. B. LIPMAN
University of California, Berkeley, Calif.
BURTON E. LIVINGSTON
Johns Hopkins University, Baltimore, Md.
HENRIK LUNDEGÅRDH
Centralanstalten för jordbruksförsök, Stockholm, Sweden
T. L. LYON
Cornell University, Ithaca, N. Y.
M. M. MCCOOL
Boyce-Thompson Institute, Yonkers, N. Y.
W. H. MACINTIRE
University of Tennessee, Knoxville, Tenn.
S. MATTSON
Lantbrukshögskolan, Uppsala, Sweden
E. A. MITSCHERLICH
University of Königsberg, Prussia
C. A. MOOERS
University of Tennessee, Knoxville, Tenn.
D. N. PRIANISHNIKOV
Petrovsko-Razumovskaia Akademia, Moscow, U. S. S. R.
THEO. REMY
Institut für Boden- und Pflanzenbaulehre, Bonn a. Rh., Prussia
G. ROSSI
Royal Agricultural High School in Portici, Naples, Italy
E. J. RUSSELL
Rothamsted Experimental Station, Harpenden, England
O. SCHREINER
U. S. Department of Agriculture, Washington, D. C.
ALEXIUS A. J. DE'SIGMOND
Royal Hungarian Joseph University of Technical Sciences, Budapest, Hungary
J. STOKLASA
Technical High School, Prague, Czechoslovakia
CHAS. E. THORNE
Ohio Experiment Station, Wooster, Ohio
N. M. TULAIKOV
Agricultural Experiment Station, Saratov, U. S. S. R.
G. WIEGNER
Landwirtschaftliche Hochschule, Zürich, Switzerland
S. WINOGRADSKY
Pasteur Institute, Paris, France

Entered as second-class matter May 12, 1919, at the post office at Baltimore, Maryland, under the act of March 3, 1879

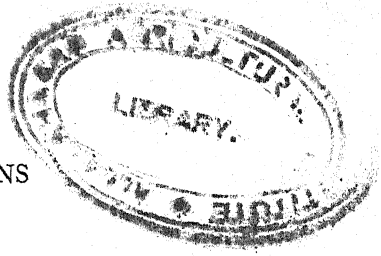
Copyright, 1954, The Williams & Wilkins Company



CONTENTS

Gintaro Daikuhara, 1866–1934 1
Indicator Plants for Measuring Soil Populations of the Root-Knot Nematode, Heterodera Marioni (Cornu) Goodey. G. H. GODFREY 3
A New Method of Measuring the Aqueous Vapor Pressure of Soils. N. E. EDLEFSEN 29
Base Exchange Studies on the Pennsylvania Jordan Field Plots. F. G. MERKLE 37
Phosphate Studies: I. Soil Penetration of Some Organic and Inorganic Phosphates. V. E. SPENCER AND ROBERT STEWART 65
First International Congress of Electro-Radio-Biology 81
Eilhard Alfred Mitscherlich. To the Sixtieth Birthday of the German Investigator. E. VON BOGUSLAWSKI 83
Root Habits of Certain Crop Plants as Observed in the Humid Soils of New Jersey. NOLAN F. FARRIS 87
Application of the Theory of Probability to the Size Distribution of Soil Aggregates. CLARK AFFLECK 113
The Carbon-Nitrogen Ratio in Relation to Soil Classification. M. S. ANDERSON AND HORACE G. BYERS 121
A Rapid Method for the Determination of Total Nitrogen in Soil. E. M. EMMERT 139
Newer Aspects of Nitrification: I. G. GOPALA RAO 143
Laws of Soil Colloidal Behavior: II. Ionic Exchange with Hydroxides. A. J. PUGH 161
Effect of Burning on Forest Soils. H. A. FOWELLS AND R. E. STEPHENSON 175
Influence of Temperature on Bacterial Nitrification in Tropical Countries. S. P. TANDON AND N. R. DHAR 183
Microbial Activities in Soil: I. Nitrogen Fixation by Azotobacter and Activity of Various Groups of Microbes in Palouse Silt Loam. S. C. VANDECAVEYE AND B. R. VILLANUEVA 191
Physiological Studies on Rhizobium: II. The Effect of Nitrogen Source on Oxygen Consumption by Rh. meliloti, Rh. trifolii, and Rh. phaseoli. R. H. WALKER, D. A. ANDERSON, AND P. E. BROWN 207
Anion Exchange: I. Adsorption of the Phosphoric Acid Ions by Soils. S. RAVIKOVITCH. 219
A Note on the Determination of Titanium in Soils. J. S. JOFFE AND L. T. KARDOS 241
Soil Profile Studies: VI. Distribution of Titanium in Soils with Special Reference to Podzols. J. S. JOFFE AND A. J. PUGH 245
Studies on Soil Protozoa. F. S. BODENHEIMER AND K. REICH 259
Profile Studies of the Coastal Prairie Soils of Louisiana: I. Exchange and Solution Properties. E. A. FIEGER AND M. B. STURGIS 267
Anion Exchange: II. Liberation of the Phosphoric Acid Ions Adsorbed by Soils. S. RAVIKOVITCH 279
Sorption of Liquids by Soil Colloids: I. Liquid Intake and Swelling by Soil Colloidal Materials. HANS WINTERKORN AND L. D. BAVER 291
The Laws of Soil Colloidal Behavior: XIV. The Electrokinetics of Hydrous Oxides and their Ionic Exchange. SANTE MATTSON AND A. J. PUGH 299
Laws of Soil Colloidal Behavior: III. Colloidal Phosphates. A. J. PUGH 315
A Comparison Between the Pipette Method and the Hydrometer Method for Making Mechanical Analyses of Soil. GEORGE JOHN BOUYOUCOS 335
The Determination of Phosphate Availability in Calcareous Soils by Electrodialysis. W. T. MCGEORGE 347

The Arsenic Content of Soils. J. E. GREAVES 355
Functional Relationships Between Soil Properties and Rainfall. HANS JENNY AND CHESTER D. LEONARD 363
Subdivision of the Upper Peninsula Experimental Forest on the Basis of Soils and Vegetation. S. A. WILDE AND H. F. SCHOLZ 383
The Microflora of Kazakstan Sands (Central Asia). E. E. PAULIE 401
Studies on Tropical Soil Microbiology. II. The Bacterial Numbers in the Soil of the Malay Peninsula. A. STEVEN CORBET 407
Book Reviews 417
The Soil-Moisture System. G. B. BODMAN AND N. E. EDLEFSEN 425
The Cunninghamella Plaque Method of Measuring Available Phosphorus in Soil. A. MEHLICH, E. B. FRED AND E. TROUG 445
Effect of the Degree of Base Saturation of a Soil on its Capacity to Fix Phosphorus in Difficultly Available Form. A. FLOYD HECK 463
The Solubility of Phosphorus in Soils from Some Illinois Experiment Fields. H. J. SNIDER 471
A Method for Determining the Degree of Decomposition that Unknown Decayed Vegetable Organic Materials Have Already Undergone in Nature. GEORGE JOHN BOUYOUCOS 477
Morphology and Genesis of the Solonetz Soils of Western North Dakota. CHARLES E. KELLOGG 483



ILLUSTRATIONS

PLATES

GINTARO DAIKUHARA

Gintaro Daikuhara (1866–1934)..... *frontispiece*

A COMPARISON BETWEEN THE PIPETTE METHOD AND THE HYDROMETER METHOD FOR MAKING MECHANICAL ANALYSES OF SOIL

Plate 1. The Dispersing Machine, Special Cup, Special Cylinder, and Soil Hydrometer.. 345

SUBDIVISION OF THE UPPER PENINSULA EXPERIMENTAL FOREST ON THE BASIS OF SOILS AND VEGETATION

Plate 1. Soils of the Upper Peninsula Experimental Forest..... 397
2. Ground Vegetation of the Upper Peninsula Experimental Forest..... 399

THE CUNNINGHAMELLA PLAQUE METHOD OF MEASURING AVAILABLE PHOSPHORUS IN SOIL

Plate 1. Growth of Cunninghamella on Soils with Different Amounts of Available Phosphorus..... 461

MORPHOLOGY AND GENESIS OF THE SOLONETZ SOILS OF WESTERN NORTH DAKOTA

Plate 1. Fig. 1. A typical view of the solonchak-complex..... 501
2. A typical view of the solodized solonetz-complex..... 501

TEXT-FIGURES

INDICATOR PLANTS FOR MEASURING SOIL POPULATIONS OF THE ROOT-KNOT NEMATODE, HETERODERA MARIONI (CORNU) GOODEY

Fig. 1. Indicator Crop Readings in Average Number of Galls per Plant on 20 Different Plots, with 10, 25, 50, 100, and 400 Plant Readings on Each Plot..... 16
2. Indicator Plant Readings on the Same Plots as in Figure 1, in Percentage of Plants Showing Infection, on the Same 25 to 400 Plants per Plot..... 18
3. Scatter Diagram, for Correlation Calculations, Showing the Curved-Line Correlation Between Gall-count Readings and Percentage-Infection Readings on 80 Separate Lots of 100 Plants Each, Where Gall Count Ranges Between 0 and 30 Per Plant..... 19

A NEW METHOD OF MEASURING THE AQUEOUS VAPOR PRESSURE OF SOILS

Fig. 1. Arrangement of Apparatus Used for Measuring Vapor Pressure of Soils..... 30
2. Electrical Connections Used in Measuring Resistance of Glass Wool Cell..... 31
3. Aqueous Vapor Pressure Curves, Permanent Wilting Percentages, and Field Capacities for a Fine Sandy Loam, a Clay Loam, and a Half-and-Half Mixture... 33
4. System for Demonstrating the Colligative Properties of Soil Moisture..... 33

BASE EXCHANGE STUDIES ON THE PENNSYLVANIA JORDAN FIELD PLOTS

Fig. 1. Typical Titration Curves..... 39
2. Relation Between pH and Saturation, Exchange H by Direct Titration..... 57
3. Relation Between pH and Degree of Saturation, Exchange H by Ammonium Acetate..... 57

PHOSPHATE STUDIES: I. SOIL PENETRATION OF SOME ORGANIC AND INORGANIC PHOSPHATES

Fig. 1. Diagram Illustrating the Meaning of the Proposed Term "Positionally Unavailable," and How it Differs from that of Fraps's Term "Physically Unavailable"..... 67

ROOT HABITS OF CERTAIN CROP PLANTS AS OBSERVED IN THE HUMID SOILS OF NEW JERSEY

Fig. 1. Rainfall and Mean Temperatures by 5-Day Periods During the Growing Season in 1930 and 1931..... 90
2. One-Half of the Root Systems of Mature Irish Cobbler Potato Plants Observed in the Fertilizer Ratio Test, 1930..... 95
3. One-half of the Root Systems of 70-Day-Old Irish Cobbler Potato Plants Grown from Various Sized Seed Pieces and Spaced at 9 inches in the Row, 1930..... 97
4. Root Systems of Mature Irish Cobbler Potato Plants Grown from Various Sized Seed Pieces and Spaced at 9 inches in the Row, 1930..... 97
5. One-Half of the Root Systems of Different Strains of Red Clover Seeded April 9, 1930..... 100
6. One-Half of the Root Systems of Various Strains of Red Clover Seeded August 25, 1930..... 101
7. One-Half of the Root Systems of Three Varieties of Corn, 1930..... 104
8. One-Fourth of the Mature Root Systems of Lancaster Sure Crop Corn Under Different Methods of Cultivation, 1931..... 105

APPLICATION OF THE THEORY OF PROBABILITY OF THE SIZE DISTRIBUTION OF SOIL AGGREGATES

Fig. 1. Graphs of Distribution Function with Three Different Values of r_m..... 116
2. Comparison Between Theoretical Synthetic Curve and Experimental Results.... 117
3. Theoretical Distribution Curves of Gold Sols Shown in Inset..... 118

NEWER ASPECTS OF NITRIFICATION: I

Fig. 1. Apparatus Designed to Show the Photochemical Oxidation of Ammonia in the Absence of Bacteria..... 145
2. Monthly Variations of the Total Radiant Energy of the Sun and the Nitric Nitrogen of the Atmosphere..... 156

LAWS OF SOIL COLLOIDAL BEHAVIOR: II. IONIC EXCHANGE WITH HYDROXIDES

Fig. 1. Original Concentration of Oxalate 2.05 m.e. in 200 cc..... 164
2. Original Concentration of Oxalate 2.05 m.e. in 200 cc..... 164
3. Original Concentration of Oxalate 2.05 m.e. in 200 cc..... 165
4. Original Concentration of Oxalate 2.05 m.e. in 200 cc..... 165
5. Original Concentration of Oxalate 2.05 m.e. in 200 cc..... 166
6. Original Concentration of SO_4 4 m.e. in 200 cc..... 168
7. Original Concentration of SO_4 4.0 m.e. in 200 cc..... 168
8. Original Concentration of SO_4 Plus C_2O_4 10.0 m.e. in 500 cc..... 170
9. Original Concentration of SO_4 Plus C_2O_4 10.0 m.e. in 500 cc..... 170

MICROBIAL ACTIVITIES IN SOIL: I. NITROGEN FIXATION BY AZOTOBACTER AND ACTIVITY OF VARIOUS GROUPS OF MICROBES IN PALOUSE SILT LOAM

Fig. 1. Microbial Development and CO_2 Production in Manured Palouse Silt Loam.... 196
2. Microbial Development and CO_2 Production in Virgin Palouse Silt Loam..... 197
3. Microbial Development and CO_2 Production in Manured and Unmanured Palouse Silt Loam at Different pH Values..... 203

PHYSIOLOGICAL STUDIES ON RHIZOBIUM: II. THE EFFECT OF NITROGEN SOURCE ON OXYGEN CONSUMPTION BY RH. MELILOTI, RH. TRIFOLII, AND RH. PHASEOLI

Fig. 1. The Ratios of the Amounts of Oxygen Consumed by *Rhizobium trifolii* in the Various Nitrogenous Media to That Consumed in the Medium Without Nitrogen 212
2. Oxygen Consumption by *Rhizobium meliloti* in Media Containing Yeast Extract.. 212
3. Oxygen Consumption by *Rhizobium meliloti* in Media Containing Ammonium Chloride, Sodium Chloride, Urea, and Alanine 213
4. The Ratios of the Amounts of Oxygen Consumed by *Rhizobium meliloti* in the Various Nitrogenous Media to that Consumed in the Medium Without Nitrogen. 214
5. Oxygen Consumption by *Rhizobium phaseoli* in Media Containing Yeast Extract. 215
6. Oxygen Consumption by *Rhizobium phaseoli* in Media Containing Ammonium Chloride, Sodium Nitrate, Urea, and Alanine 216
7. The Ratios of the Amounts of Oxygen Consumed by *Rhizobium phaseoli* in the Various Nitrogenous Media to that Consumed in the Medium Without Nitrogen 216

ANION EXCHANGE: I. ADSORPTION OF THE PHOSPHORIC ACID IONS BY SOILS

Fig. 1. Adsorption of Phosphoric Acid Ions by a H-Soil and a Ca-Soil (from Esdraelon Valley) from Solutions of Various Concentrations 228

STUDIES ON SOIL PROTOZOA

Fig. 1. Number of Soil Protozoa 263

ANION EXCHANGE: II. LIBERATION OF THE PHOSPHORIC ACID IONS ADSORBED BY SOILS

Fig. 1. Effect of the Addition of $Ca(OH)_2$ on the Liberation of PO_4 in a H-Sandy Soil.... 281
2. Effect of the Addition of $Ca(OH)_2$ on the Liberation of PO_4 in a H-Clay Soil..... 284
Fig. 3. Effect of the Addition of NaOH on the Liberation of PO_4 in a H-Sandy Soil..... 287
4. Effect of the Addition of NaOH on the Liberation of PO_4 in a H-Clay Soil..... 287

SORPTION OF LIQUIDS BY SOIL COLLOIDS: I. LIQUID INTAKE AND SWELLING BY SOIL COLLOIDAL MATERIALS

Fig. 1. Apparatus for Measuring the Liquid Sorption and Swelling of Soil Colloids..... 292

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XIV. THE ELECTROKINETICS OF HYDROUS OXIDES AND THEIR IONIC EXCHANGE

Fig. 38. The Adsorption of the Oxalate Ion by Aluminum, Ferric, Titanium, and Stannic Hydroxides 309

THE DETERMINATION OF PHOSPHATE AVAILABILITY IN CALCAREOUS SOILS BY ELECTRODIALYSIS

Fig. 1. Typical Examples of the Effect of Amperage on Phosphate Extracted by Electrodialysis from a Poor Soil and a Good Soil 349
2. Relation Between Neubauer Value, Milligrams PO_4 Removed from 100 Gm. Soil by 100 Rye Plants, and Milligrams PO_4 Extracted from 2 Gm. Soil by Electrodialysis with 0.2 Ampere Flow of Current 350

FUNCTIONAL RELATIONSHIPS BETWEEN SOIL PROPERTIES AND RAINFALL

Fig. 1. Chestnut Soils, Chernozems, and Prairie Soils Form Narrow Belts Extending from North to South 366
2. Depth of Carbonate Zone 367
3. Nitrogen-Rainfall Function I 368

4. Nitrogen-Rainfall Function II 370
5. Amount of Inorganic Colloid as Affected by Rainfall 371
6. Clay-Rainfall Correlation 372
7. Soil Acidity Relationships. Change in pH and Exchangeable H Ions with Rainfall 373
8. Saturation Capacities of the 0–10 Inch Surface Samples 374
9. Relation Between Exchangeable Cations and Rainfall 375
10. Generalized Sigmoid Curve Showing an Inflection Point in the Semi-Arid Region and a Maximum Under High Rainfall 377
11. Relative Soil Property-Rainfall Curves Demonstrating That Various Soil Characteristics Exhibit Different Rates of Formation 378

SUBDIVISION OF THE UPPER PENINSULA EXPERIMENTAL FOREST ON THE BASIS OF SOILS AND VEGETATION

Fig. 1. Schematic Representation of Typical Soil Profiles, Showing the Minimum and Maximum Depths of the Horizons 385
2. Soils and Forest Cover of Virgin Portion of the Experimental Forest 386

STUDIES ON TROPICAL SOIL MICROBIOLOGY: II. THE BACTERIAL NUMBERS IN THE SOIL OF THE MALAY PENINSULA

Fig. 1. Fluctuations in Bacterial Numbers on Block 15 of the Sungei Buloh Experiment Station During the Conversion of Virgin Forest into a Rubber Plantation 409

THE SOIL-MOISTURE SYSTEM

Fig. 1. Typical Vapor-Pressure Curves for Sand and Clay, Showing Wilting Percentages and Field Capacity 427
2. Diagram of Forces Acting on Elemental Volume of Water 429
3. Diagram of Water Wedge to Illustrate Forces Acting on Soil Moisture 430
4. A System for Demonstrating the Colligative Properties of Soil Moisture 433
5. Relationship Between Vapor Pressure and Capillary Potential of Water at 20°C. .. 435
6. Relationship Between Time Since Disappearance of Water Table from Soil Surface and Moisture Content of Soil, Expressed as Surface Inches 437
7. Transmission of Water Through Saturated Sands and Soils 439
8. Quantity of Water Transmitted Through Soil Planes in Surface Inches Per Day as Related to Depth and Time 440

THE CUNNINGHAMELLA PLAQUE METHOD OF MEASURING AVAILABLE PHOSPHORUS IN SOIL

Fig. 1. Relation of Lateral Growth of Cunninghamella on 10 Different Soils Before and After the Addition of 10 Increments of Available Phosphorus 450

EFFECT OF THE DEGREE OF BASE SATURATION OF A SOIL ON ITS CAPACITY TO FIX PHOSPHORUS IN DIFFICULTLY AVAILABLE FORM

Fig. 1. The Relation of Hydrogen-Ion Concentration to Phosphorus Fixation in Miami Silt Loam 465
2. The Relation of Exchangeable Calcium to Phosphorus Fixation 465
3. Relation of Exchangeable Base (Calcium) to the pH Values of Miami Silt Loam and Waipio Soil 466
4. Exchangeable Calcium Retained by Miami Silt Loam and Waipio Soil When the Calcium Saturated Soils are Leached with Carbonated Water 467
5. The Effect of Exchangeable Calcium and Exchange Material on the Recovery in Readily Available Form of Phosphorus Applied to Waipio Soil 469

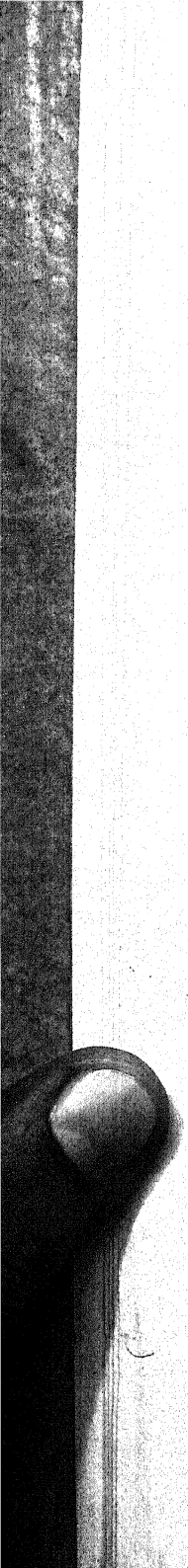
THE SOLUBILITY OF PHOSPHORUS IN SOILS FROM SOME ILLINOIS EXPERIMENT FIELDS

Fig. 1. Solubility Curves Showing the Effect of Time Upon the Amount of Phosphorus Extracted from Different Soils 474

MORPHOLOGY AND GENESIS OF THE SOLONETZ SOILS OF WESTERN NORTH DAKOTA

Fig. 1. Sketch Map Showing the General Features of Vegetation and Climate for Western North Dakota 485
2. Sketches Showing Some of the Principal Types of Profiles Mentioned in the Text. 486
3. Cross Section, Made to Scale from Level Notes, Through the Puffed Spot in the Solonchak-Complex 489
4. Cross Section, Made to Scale from Level Notes, Through an Eroded Spot on the Solonetz-Complex 493
5. An Outline of the Cycle of Evolution of the Alkali Soils in Western North Dakota. 497







GINTARO DAIKUHARA (1866–1934)

ALLAHABAD AGRICULTURAL INSTITUTE
LIBRARY.

Gintaro Daikuhara

1866–1934

With the sudden death of Dr. Gintaro Daikuhara, on March 9, not only Japan but the world lost one of its pioneer soil scientists, renowned for his work on soil acidity and for his method of determining the lime requirement of soils.

Doctor Daikuhara was born in 1866, in the Nagano Prefecture, Japan. He was graduated from the College of Agriculture, Tôkyô Imperial University, and, a year after his graduation, joined the staff of the Imperial Agricultural Experiment Station where he served for 27 years. In 1908 he was appointed lecturer at the Tôkyô University and in 1910 received the degree of doctor of agriculture (Nogaku-Hakushi). He was then sent by the government to study for 2 years the science of fertilizers in Europe and in America. While abroad, he served on one of the exhibition juries at the world exposition which was held in Italy, and also attended the Eighth International Congress of Applied Chemistry, which was held in Washington and New York in 1912. Returning to Japan, he served as one of the judges at the Patent Office and continued his work on soils and manures and on various other agricultural chemical problems.

In 1921 Doctor Daikuhara was appointed to an additional position as Professor of Kyûsyû Imperial University and also to the Board of Trustees of the University. Two years later he became Director of the Agricultural Experiment Station, Province of Korea, where he contributed greatly to the improvement of agriculture. In 1926, he was made President of Kyûsyû Imperial University. In 1929, he resigned in order to accept the presidency of Dosisya College. He passed away while actively engaged as the President of Dosisya.

While occupying various official positions, Doctor Daikuhara was a loyal member of many scientific and educational societies, to all of which he gave his hearty support. The International Society of Soil Science, in particular, enjoyed his earnest and valuable coöperation. He published in Japan and abroad many notable papers reporting the results of his investigation on soil acidity and on a new method for its determination. This method is now widely used. His book "Lectures on the Science of Soils" (Dojyôgaku-Kôgi) is the standard work on soils in Japan.



INDICATOR PLANTS FOR MEASURING SOIL POPULATIONS OF THE ROOT-KNOT NEMATODE, HETERODERA MARIONI (CORNU) GOODEY[1]

G. H. GODFREY

University of Hawaii

Received for publication August 23, 1933

In experimental work and practical plant culture in which the root-knot nematode is of major interest, it is often highly desirable to obtain a measure of the degree of soil infestation by this organism. The method used at present by this laboratory for the purpose is to plant a highly nematode-susceptible crop in the soil to be tested, and to record the amount of nematode infection, usually in terms of root-gall count. Many studies on the effects of all manner of soil treatments for nematode control have applied this method in part, but this paper records the refinement of the method to a higher degree of accuracy and usefulness than has heretofore been reported. It is based upon a careful statistical study of various phases of the problem.

LITERATURE REVIEW

The literature is lacking with respect to reliable and practical means of obtaining a measure of variations in the population of this nematode in field soils. Very few studies incorporating careful measurements of this sort, at all commensurate with the importance of the root-knot problem, have been made. Cobb (4) has described in great detail a method for obtaining a general nematode census of soils. This involves the taking of a number of representative soil samples, compositing them, taking an aliquot part of the composite sample, separating the contained nematodes by screening or gravitation methods, identifying and counting them, and on the basis of these counts, calculating an estimate of the population per acre of the different species. After describing the method, Cobb lists its various fields of usefulness, pointing out the importance to the investigator of being able to determine the effects of the various changes to which a field may be subjected (including specific control measures) on the nematode population of a field that is under observation.

A number of investigators have made statistical studies of nematodes of other species than *H. marioni* in the soil, by Cobb's method or some modification of it. Many of these deal with *H. schachtii* Schmidt, which is easily isolated by virtue of the so-called brown cysts which are relatively easily separated from the soil. Thorne (32, 33) uses the washing and screening method in making counts of *H. schachtii* in the western states and records his counts by season and by soil depth. Morgan (26), in England, uses a flotation method for freeing

[1] Published with the approval of the Director as Technical Paper No. 63 of the Experiment Station of the Association of Hawaiian Pineapple Canners, University of Hawaii.

The writer is adopting for this organism the nomenclature of Dr. T. Goodey (*Jour. Helminthol* 10: 21–28. 1932) in preference to the old names, *Heterodera radicicola* (Greeff) Müller and *Caconema radicicola* (Müller) Cobb, which have been shown to be erroneous.

the cysts from the soil and makes counts from representative soil samples. Goffart (18) uses a similar method, as do also several others in Germany. Triffitt (35) uses Morgan's method for field studies. In her experiments (34) on the effect of mustard in reducing the amount of actual infestation of potato roots with this species, in pot studies in the greenhouse, she removes the root-bound soil from the pots and makes her comparative estimates of degree of infestation on the basis of counts of female nematodes, white and brown, on the roots that were visible on the surface of the ball of earth and the interior of the pot. Perhaps the most complete and exhaustive statistical studies on soil infestation by *H. schachtii* are those by Smith and Prentice (30), Smith (28), Smith and Miles (29), and Buckhurst and Fryer (2), in England. They attempt to correlate, by sound mathematical methods, the actual counts obtained with various physical factors of the environment and with intensity of disease produced and crop yields. They give adequate consideration to the problems of standard error in statistical analyses and to field and laboratory errors in making counts. The writer suspects that in the work of Smith and his colleagues one of the unknown factors which vitiates expected results is the counting of nearly empty "brown cysts" of uncertain age, instead of living material alone. Buckhurst and Fryer consider this and include in their counts only cysts shown to contain living larvae.

Most students of the soil-inhabiting nematodes use the washing and screening method in one form or another for isolating the nematodes from the soil. It is generally recognized, however, that an accurate direct soil count is exceedingly difficult to make for organisms so small as the larvae of *H. marioni* and *H. schachtii*. Thorne (32, p. 6) even includes the relatively large males of the latter species in this category.

Another method, distinctly different from the actual soil census, is that of the use of a nematode indicator crop. This method has been used by the writer (11) to determine the effects of different temperatures on the capacity of the nematode to infect plants, and again (10) more directly as a measure of soil infestation, in studying the depth distribution of nematodes in soils. McClintock (25) has applied the same method roughly for testing the soil of nurseries for the presence of the root-knot nematode. Many other investigators have made use of the basic idea whenever they have treated soil for nematode control and have planted a crop for the purpose of determining the effectiveness of the treatment. Byars (3) reports results of experiments on the application of hydrocyanic acid gas on the basis of percentage of crop plants affected in the planting immediately after the application. DeOng and Tyler (7) report results from experiments with potassium xanthate on the basis of zero, light, and heavy infection of succeeding crops. Watson in various papers (37, 38) reports results from several different treatments on the basis of freedom of ensuing crops from nematode infection, though he does not record actual figures by which an accurate quantitative measure of control could be made. Neither do Hodson and Gibson (21), who report merely the presence of heavy nematode infections in calcium cyanide treated and untreated plots alike. Newhall (27) reports, for some of his experiments, merely the presence or absence of galls, using yield results as the only criterion of effectiveness of treatments, for most of his work. Guba (20) reports percentages of plants with zero, light, moderate, and severe infection. Recently Johnson and Godfrey (23) and Godfrey (12) reported the effects of chemical treatments of soils for nematode control, using the quantitative methods presented in this paper.

BASIC CONSIDERATIONS IN HETERODERA MARIONI POPULATION STUDIES

Where nematode root-knot is an important factor in crop production, the growing crop itself where present gives to some extent an indication of the degree of soil infestation. Frequently the above-ground portion of the plant tells the story by its general unhealthy growth, its dwarfed condition and "off-color," and frequently by its early death. The front cover page of the

U. S. Department of Agriculture general bulletin on root-knot (9) shows a cowpea field in which practically all plants are dead, without a yield, due to root-knot. Less severely infested fields can be determined by pulling an occasional plant and examining it for the abundance of the typical nematode galls.

It is usually in relation to the unplanted field—the field under consideration for planting or in actual process of preparation for planting—that the question arises as to its degree of infestation and therefore its potentialities for success or failure of the ensuing crop. It goes without saying that, immediately following a heavily infested crop, a newly plowed field will be uniformly 100 per cent infested; that is, every square foot of the soil will produce plants showing the presence of galls. In the absence of growing susceptible plants, the nematode population begins immediately to decrease. The writer's experience has shown this to obtain at the start, at a rapid rate. Natural enemies in the soil and various physical factors of the environment, some of which have been considered in some detail (14, 17, 22), show their effects by a quick drop in effective nematode population. Specific studies have shown, however, that many nematodes will survive over a long period. One condition or another, perhaps a pocket in the soil with a more or less woody root system containing the remains of an earlier infection in which decay processes have been delayed (20, 24), results in survival of a heavier population in one spot than in another.

If any program of nematode reduction has been followed, such as clean fallow, the growing of immune rotation crops, or the use of chemicals, infestation will be, if not completely eradicated, at least very much reduced. A chance susceptible volunteer crop plant or a susceptible weed, however, will become infested, and within a month or two that spot in the soil will have had a high population restored. Cobb (4) has suggested the likelihood of irregularities in degree of infestation in different parts of a field. The writer has found this condition to be very common. This, then, is the condition usually found when one is interested in obtaining a reading on soil infestation to determine the effectiveness of a treatment.

An acre field, 43,560 square feet, contains in its upper foot, which is where most of the effective nematodes are to be found, something over 325,000 gallons of soil. The problem before the writer was to determine the most effective and at the same time practicable means of adequately sampling such a field. He first tried Cobb's (4) direct soil census method. Hawaiian soils are extremely high in colloidal material. The finer-meshed screens, upon which *H. marioni* larvae were to be found, if at all, hold large quantities of fine soil. When placed in beakers, such soil, even after repeated washings, immediately makes the water turbid by the further release of colloidal matter. Settling and pouring off the supernatant liquid is not effective in removing it, as the soil is so fine that settling is very slow and the nematodes inevitably fall to the bottom at the same time. Screening the turbid water again merely means the constant repetition of the process. Every such screening introduces error in the probability of loss of nematodes. Making counts directly, in turbid

water, is almost impossible, and if larvae are detected at all, counts obtained invariably have a high percentage of error. Unless samples are very small, hours and even days are required for complete readings.

In Cobb's paper no data are given on the efficiency of recovery of known concentrations of larvae or eggs of Heterodera species from the soil. In attempts to supply such information from Hawaiian soils, very unsatisfactory data were obtained. Variations in recovery ranged from 0 to 40 per cent, even with initial soil samples as small as 400 cc. (almost exactly 1 3-millionth part of an acre foot) and with counts ranging from 5 to 100 larvae inserted into such samples. The occurrence of a single larva in such a 400-cc. sample would mean about 10 in a gallon or about 80 in a cubic foot (28.3 liters). Much fewer than 80 per cubic foot are likely to be highly significant in building up a destructive population in a growing field. Yet, should the laboratory helper fail to find that single larva in 400 cc. of soil, the determination would be zero for the area represented by that sample. In other words the direct count method is not reliably applicable even as a detector of infestation in the lower concentrations and is far from accurate as a count in the more heavily infested soils.

Governed by his experiences along these lines, the writer gave increased attention to the possibilities of the indicator plant as an actual measure of the extent of soil infestation. Without condemning the direct soil census method, which is absolutely essential for a study of the general nematode population of soils, he early abandoned it, for *H. marioni* estimates, in favor of the much simpler, and for most purposes entirely adequate, indicator plant method, an exposition of which follows.

EXPLANATION OF THE INDICATOR CROP METHOD

The method calls for the planting of a highly nematode-susceptible plant in the soil to be tested, preferably under optimum conditions for growth and for infection, and examining root systems for extent of gall formation. For field tests, obviously, it can be used only in the growing season, and only when moisture and other conditions are favorable for germination of seed (if the plant is to be seeded), for root development, and for nematode infection. At any season field samples can be taken and removed to the favorable conditions of the greenhouse, where the test can be made in pots, as was done in earlier studies by the writer (10).

The choice of plant is determined by several factors. Seedling tomato plants (*Lycopersicon esculentum* L.) are highly satisfactory for some purposes. They must have been grown in nematode-free soil, and should be relatively uniform in size and vigor, in order that all plants make approximately the same amount of root growth during the period of exposure to infection. Planting directly by seed has proved to be most satisfactory for our needs, as this makes for uniformity and for economy when large numbers are to be con-

sidered. The satisfactory seed crop should have large seeds, as this makes more certain quick development of a large plant, with root system of sufficient spread and penetration, in the limited time available. Soil temperature is another factor. If that is relatively low, as it is even under Hawaii conditions early in the spring (13 to 16°C.), then a low temperature loving plant such as English pea (*Pisum sativum* L.) is desirable. Satisfactory indicator crop readings can not be taken at a temperature below 13°C., which is approximately the minimum for activity of the root-knot nematode (11). After the soil becomes relatively warm (19°C. or higher), a susceptible plant with higher temperature requirement, such as cowpea (*Vigna sinensis* L.) or soybean (*Glycine max* [L] Merr.) is better. In all the suggested plants primary infection becomes evident as relatively distinct galls, and in cases of medium soil infestation, galls are fairly uniformly distributed through the root system. Heavily infested terminal galls are not the common thing as in pineapple and some other plants.

The application of this method is based upon a count of the number of primary infections, manifested by gall development, that appear on the roots of the indicator plant during the period in which its roots are exposed to infection by growing in that particular soil.

The method can be used as a means of estimating numbers of infective larvae in the soil. It is applicable in practice as a measure by which different plots or portions of a field can be compared with one another. It is comparable in this respect to the dilution-culture method of counting bacteria, in which method it is recognized that the individual colonies of the culture-plate (which are the only things actually counted), may have arisen frequently from clusters of two or more bacteria clinging together. Each gall frequently contains two or more developing nematodes. For practical purposes, however, it has been considered that if two plants are growing under approximately the same conditions and have developed approximately the same extent of root growth, and one of them has twice as many root galls as the other, the ratio of soil infestation at the time the indicators were planted was probably very close to 2 to 1. Statistical studies herein reported justify this assumption.

Root-knot counts for this purpose are strictly applicable only to primary galls. Plants which have been exposed to second generation larvae and which contain compound galls as well as new generation small galls cannot be rated so satisfactorily as an indication of degree of soil infestation, on the basis of gall counts, since large galls must be given much greater weight than small ones; furthermore, new generation galls are not a measure of original infestation.

The fact that size of galls varies greatly, even in primary infections, is taken into consideration in making counts. Since the mature female nematode is approximately 1 mm. in diameter, each millimeter of gall length is counted as one. Thus, a single gall 3 mm. long would be counted as 3, in counting gall

numbers. Such a gall contains at least three nematodes and probably more, which places it on a par with the single gall which contains one or more, as will be seen in the following report of exact studies.

All environmental conditions must be favorable for both the host plant used and for the activity of the nematode. Temperature is one of the most important of these factors. The writer has previously shown that, given soil of uniform infestation, the amount of infection that takes place is greatly dependent upon temperature. His conclusions (11, p. 252) are very definite upon this point. Tyler (36) has shown that the nematode passes through its complete life cycle in minimum time at about 28°C. The range of temperatures favorable for activity, as manifested by heavy infections in susceptible plants, however, is high—from 18 or 19° to 30°C. or higher (11). Other things being equal, for indicator plants the lower portion of this range is preferable to the higher, in that, with the increased length of time available before reproduction takes place, the root system of the plant permeates the soil more efficiently than during the shorter period at a higher temperature. In the same paper, the writer has concluded that, given favorable temperature, any moisture condition favorable for plant growth will permit of root-knot nematode activity. In the light of more recent knowledge on soil moisture relations it would seem that his soil moistures were not satisfactorily controlled. It is probable that all his higher moistures, 60 per cent and up, of "moisture holding capacity" were in excess of the present standard of "moisture equivalent" moisture (6). There is no way of checking his standards with moisture equivalent standards without having exactly the same soil mixtures. Furthermore it is now recognized that the lower degrees of moisture content could not possibly have been maintained with any uniformity, with growing plants in them. The desirability of further work with controlled moisture is indicated. Greatest nematode activity appears to take place, however, at moistures most favorable for plant growth, and this would seem to be a safe criterion for procedure with indicator plants. Soil acidity, as reported in another paper (13), does not appear to be a factor of much importance. As a rule, in comparing plots or portions of a field as to degree of nematode infestation, all of these factors will be approximately the same, and therefore may be considered to be controlled.

EXPERIMENTATION

To develop a basis for judgment as to the reliability of the gall-count method in making estimates of degrees of soil infestation at any particular time, several test plantings and nematode counts were made. Although the results are far from completely satisfactory and much experimental work remains to be done, the accomplishments up to the present time add much to the security with which the method can be used.

AGRICULTURAL LIBRARY

Accuracy of gall counts

A number of factors making for error in actual counts enter into consideration. Roots broken off in removal of plants, very recent infections with consequent slight swelling or absence of visible swelling of the root, extremely heavy infections resulting in compound galls whose numerical value on the standard length-of-gall basis is difficult to estimate, dwarfing of root systems due to extremity of infection, uncertainty as to actual numbers of nematodes contained within galls: these are some of the conditions that make for inaccuracies in counts.

Where infections are so heavy as to bring about uncertainty, the evidence is sufficient for an immediate classification as "infestation extreme." As to the other points, in an attempt to establish some definite criterion as to their importance a detailed statistical study was made of indicator crops from certain field plots.

For the experimental determination of numbers of galls on roots lost on removal of plants, the indicator plants came from three separate sources and fell naturally into three classes according to degree of soil infestation—heavy, medium, and light—and they were so studied, each lot by itself. The plants, selected at random were removed from the soil at the expiration of the usual period, approximately 30 days, according to regular practice. Following the removal of each plant to be studied in this connection, the soil in which it stood was carefully sifted and all broken roots picked out. These were wrapped with the original plant. In all cases where obviously a large proportion of the root system had been broken off in removal, the plant was discarded as in regular practice.

In the laboratory all roots were thoroughly washed, and readings were taken on each plant separately, in numbers of galls on roots still attached and numbers of galls on roots that had become broken off in removal. In ordinary practice only the galls on the roots of the main part of the plant just as it is removed from the field are counted. This figure, then, was taken as 100 per cent, and the "error" in count, as measured by gall count on roots broken off on removal, was recorded as a percentage of the basic count. Likewise in one case only, that of heavily infected plants, the total number of nematodes contained in the roots was determined, using the clearing method described in another paper (16, p. 327). The results for the three lots of plants, grouped according to degree of infestation, in averages per plant, are as follows:

Heavy, 21 plants, basic count, 643 galls; "loose root" error, 31.1 ±2.3 per cent.
Medium, 25 plants, basic count, 187 galls; error, 34.3 ±3.3 per cent.
Light, 14 plants, basic count, 9.86 galls; error, 39.1 ± 5.5 per cent.

The total nematode count in the first lot was 1,545 average per plant, or 2.404 times the basic gall count. The variations were so high in every lot that they can not be considered as separate homogenous groups. Furthermore the

number of cases in each lot was so low that little significance can be attached to these figures. It is interesting to note, however, that the loose-root error was least in the heavy infestation lot and greatest in the lot with light infestation. This observation is again referred to in another section of this paper.

The heavy infestation lot ranged in basic gall count from 207 to 1,345 galls, and in total nematode count from 399 to 3,442. By way of further study on this lot alone, plant by plant correlations were determined between (*a*) basic gall count and (*b*) total gall count, using step intervals of 100 for both counts; between (*a*) basic gall count and (*c*) total numbers of contained nematodes, using a 200 step interval for the latter; and between (*b*) total gall count and (*c*) total nematodes. The *ab* correlation was .801 ±.053. The regression equation for determining total gall count from basic gall count is

$$X = 1.384\ Y + 114\ (\pm 141)$$

A test of this equation on the correlation table showed a fairly high reliability, though the probable error obviously is high.

On the same group of plants the *ac* correlation is .912 ±.025 and the *bc* correlation, .925 ±.022. The two are very close together. The amount of time saved by removing only the main part of the root system instead of carefully removing all broken roots as well is tremendous. Since the correlation with count of nematodes "picked up" is so high and so nearly equal to that when the entire root system is included, the simpler process would appear to be a very reliable method of measuring plot or field differences in amount of initial infection that actually occurs. The regression equation for the *ac* correlation is

$$X = 2.85\ Y - 248\ (\pm 212)$$

When applied to the correlation table, 3 plants in the 900 group averaging in basic gall count 926, and in actual nematode count 2,670 gave a calculated reading of 2,391 ±212. A lower infection group gave a calculated reading for X of 885 ±212 as compared with the actual reading of 743. This, again, is only fairly reliable though sufficiently so for most purposes. Obviously, for any extensive application, this basic principle for nematode estimates, which is only indicated here, should be refined by the development of a similar correlation table based upon a very much larger population of plants, perhaps 1,000 or even more. Further refinement of the method of excavating roots for the basic gall count is also under consideration, as discussed in another section of this paper. The results here analyzed were from indicator plants removed by laborers without special training. Plants that were obviously badly broken, with more than 50 per cent of the roots left in the soil (about 10 per cent of them in this case), were discarded when examinations were made for number of galls.

The question might arise as to the accuracy possible in making superficial counts of galls as against the completely accurate histological method. What

is the percentage of error caused by missing galls that are not clearly evident? Actual count on the same material as that used in the foregoing statistical study, in which such galls, made evident only by the clearing method, were recorded separately, showed only 4.28 per cent in this category. This percentage is so low that it can very well be disregarded, particularly as the calculated correlation between missed galls and missed nematodes in the entire plant is .882, almost the same as the *ac* correlation. With greater refinement in other parts of the technique an additional factor can be inserted for this error, as well, if it seems desirable.

Additional data from gall counts on this same material are recorded here as a matter of general interest, though they do not contribute particularly to the problem of population estimates, except in the way of a better understanding of it. Tabulation of the counts of galls and of nematodes on the 21 plants showed that 63.04 ±2.29 per cent contained only a single nematode, the balance containing two or more. The relatively high percentage containing two or more, some of them with three, four, or five nematodes, is of course, responsible for the high ratio 2.40 to 1 for numbers of nematodes actually contained in the entire root system to numbers of galls on attached roots.

Efficiency in detecting infestation

Granting that the principle thus far expounded is a sound one, and that the indicator crop method with the greater refinement that is contemplated will give a fair estimate of the amount of infection that actually takes place in a given soil, the question naturally arises as to how efficient the method is in detecting the total nematode population present in the soil. In other words, what proportion of the nematodes present in the soil at a given time will be detected by a single planting of an indicator crop? Actual results of various studies are reported here as throwing light on that point. In a trap crop experiment reported by Godfrey and Hoshino (15) an average, from triplicate tests, of over 3,000 galls were counted on a first planting of a "trap" crop in gallon containers. This first planting was removed before any reproduction had taken place. A second planting showed an average of 13 galls only. Two subsequent plantings showed 25 more, making 38 in all or slightly more than 1 per cent of those detected by the first planting. This is a very small error indeed, well within the range of probable error, and can very well be neglected in estimating the total *effective* nematode population.

Another experiment of a different nature likewise gives significant information. In a test on depth distribution of nematodes in the field, gallon samples of soil were taken from different depths. All samples were planted to a suitable indicator. One set from each depth was left for 30 days only and a second set for 60 days. The second set naturally would be expected to show a higher count than the first, since it would contain galls produced by second-generation larvae. This was true in 17 cases out of 40, 4 giving identical readings in both. In 19 cases in which the 30-day reading was zero, 2 of the

60-day readings were likewise zero, 13 showed only 10, or fewer galls, and the remaining 4, only about 20. This shows that most of the original infestations which read zero in the first reading, while not actually zero for infection, were very low indeed to have given these low readings even after reproduction had occurred. A single maturing female, or at most only two or three, may have been present in each case. The 30-day reading, or the true indicator plant method, then was successful in showing sufficiently accurately the presence of infestation in 52.5 per cent of the soil samples, and the absence of infestation in 5 per cent. In the remaining 43.5 per cent of the cases no infestation was indicated when actually just a trace was present. It so happened that in some cases the growth of indicator plants in these particular soils was very poor. In later refinements of the method, in which good growth is one of the essentials, brought about by better control of soil texture, fertility, and moisture, much higher accuracy has been obtained. Again, some of the containers for the 60-day reading may have contained, by chance, living nematodes where the first did not.

It is recognized that with both tests referred to, since the roots of indicator plants were confined within the space of a single gallon, chances were much greater of catching all the contained nematodes than under field conditions where the "range" of a root system is nearly an entire cubic foot.

A complete consideration of the efficiency of the trap crop called for additional work, particularly on percentages of total populations that may be caught in a single planting under adequately controlled conditions. In July 1932 a series of sixty 5-gallon (20-liter) iron paste-buckets was prepared for this study by filling all buckets with typical pineapple field soil which had previously been spread in a thin layer in the sun to dry for several days. Previous experience (14) had shown that this was a very satisfactory means of killing all the root-knot nematodes that were present in the soil, in whatever form. At the same time such soil was more favorable for subsequent plant growth than is steam-sterilized soil, which frequently appears to have a toxic effect. The containers were arranged on tables in the greenhouse. They were then inoculated with counted numbers of freshly hatched larvae placed in drops of water in several different holes at approximately medium depth. The rates of inoculation were as follows: lot A, 20 containers, 50 larvae each; lot B, 20 containers, 500 larvae each; lot C, 20 containers, 2,000 larvae each. Whippoorwill cowpeas, a highly susceptible variety, were then planted and upon sprouting in 2 or 3 days were thinned to one vigorous plant near the center of each container. Relatively uniform favorable moisture conditions were maintained, and the plants grew well. At 30 days after planting, lots A and B were removed carefully, each plant being kept separate with its entire root system. Lot C was left growing a few days longer, and upon examination it was evident that definite secondary infection had taken place from the progeny from primary infections. The results from lot C, therefore, can not be considered in this study. The roots from lots A and B were thoroughly washed

and then killed with Flemming's killing solution, dehydrated through a series of alcohols, and cleared in clove oil according to methods previously reported (16) It was desired to obtain not only an accurate gall count, but a complete

TABLE 1

Efficiency of indicator-crop recovery of nematodes from known magnitudes of initial soil infestation in 5-gallon containers

LOT A 50 LARVAE PER CONTAINER			LOT B 500 LARVAE PER CONTAINER		
Can number	Number of galls	Number of nematodes	Can number	Number of galls	Number of nematodes
1	13	13	1	121	131
2	11	12	2	115	121
3	6	6	3	188	216
4	11	11	4	70	80
5	9	10	5	99	110
6	10	11	6	107	110
7	12	12	7	177	186
8	10	10	8	156	162
9	16	17	9	173	186
10	15	15	10	189	285
11	13	13	11	129	131
12	4	4	12	98	103
13	9	9	13	118	123
14	11	12	14	150	169
15	9	11	15	99	101
16	10	11	16	129	142
17	9	9	17	133	164
18	13	15	18	121	133
19	10	11	19	140	196
20	10	10	20	124	158
Average	10.55 ±0.40	11.10 ±0.41		131.8 ±4.73	150.35 ±7.63
Ratio $\frac{\text{Nematodes}}{\text{galls}}$	1.05			1.14	
Per cent recovery	22.2			30.07	
Ratio $\frac{\text{original nematodes}}{\text{galls}}$	4.74			3.79	

Correlation between gall count and nematode count, for entire 40 plants, .933 ±0.014

count of nematodes contained within the roots as well. Galls were counted according to the usual method of evaluating larger ones according to their length in millimeters. Since this is the first study of the kind reported, the plant by plant observations are recorded in table 1.

Attention is called to certain significant observations in this table. With the lower initial nematode infestation 11 of the 20 plants, or 55 per cent, showed throughout the root system only a single nematode to a gall (on the 1 mm. to a gall criterion, as explained on page 7). All the other nine plants had one or more galls containing more than one nematode. The discrepancy between gall count and nematode count for the entire 20 plants, however, was only 5 per cent. With the higher initial nematode population in lot B, no plants whatever showed throughout the single-nematode-to-a-gall condition, and the discrepancy in count was 14 per cent.

Likewise the per cent recovery of original nematodes was greater in the case of higher initial infestation. There would appear to be greater ease in penetration of roots with the joint action of several larvae, as was suggested as a possibility in a previous paper (16, p. 328). Whether or not this situation—higher percentage recovery with higher initial soil infestation—would continue through a long series of magnitudes of initial soil infestation, could be determined only from a very large scale experiment with sufficient replications and accurately controlled conditions. If such should prove to be the case, then a curved line correlation between gall count and recovery of nematodes could be established. A tabulation, then, and the construction of such curve, would permit of making a fairly accurate estimate of original nematode content of the soil. According to Garrett (8, p. 211) and other statisticians, no regression formula can be constructed that would fit all cases, as can be done with a simple straight-line correlation.

In this test, as might be expected from the fact that nematode count is as a rule only slightly in excess of gall count, the correlation between total gall count and total actual nematode count is high, .933 $\pm$0.014, for the total population of 40 plants. Since with the count of 50 initial larvae in the soil the gall count average was 10.55 $\pm$0.40 (the low probable error indicating relative uniformity), the true number of nematodes constituting primary soil infestation is 4.74 times as great as the gall count. From the previous experiment (p. 9) it was calculated that low gall count averages on roughly removed plants could be transformed to approximate gall counts on the entire root system by multiplying by the factor 1.39. By multiplying any low gall count reading by 1.39 and then by 4.74, one would arrive at an approximation to the actual soil infestation in the volume of soil reached by the roots of the indicator plant, approximately 1 cubic foot. (The containers used in the second experiment, 5 U. S. gallons in capacity, or approximately $\frac{5}{8}$ cubic feet, usually showed some matting of the roots of the indicator plant at the sides and bottom at the end of the 30-day growth period. The readings obtained are therefore considered to be approximately the same as would be obtained in an entire cubic foot of soil.) The two factors combined, 1.39 and 4.74, make a joint factor of about 6.6. To illustrate the estimation of a nematode population, then, supposing the average gall count on a number of roughly removed indicator plants to be 7.57, multiplying by 6.6 would give 50 nematodes as the population per cubic foot, or 2,178,000 per acre foot of soil.

With the initial infestation 10 times as great, the regression formula, $X = 1.384\ Y + 114$ (see p. 10), would probably give greater accuracy in estimating total gall count than would a single factor (unless a table were developed, based upon a large number of actual counts for each of several different magnitudes). The final factor, as shown in table 1, for a population of 500 larvae per cubic foot, being 3.79, 3.79 X (however X is determined) would represent the number of nematodes per cubic foot, and this multiplied by 43,560 would give the population per acre foot.

The data are insufficient to extend estimates of factors beyond these two populations except by rough interpolations. However, the data give a sufficient basis for rough approximations within the range usually encountered in nematode reduction experiments, and, until more complete data are available, should constitute a usable "tool" for measurements in such experiments. Differences can be recorded in terms of direct gall counts or in populations per acre foot or other unit of soil volume. The roughness of the approximations is recognized, particularly where soil and seasonal differences enter into consideration. Further refinement of the method is clearly called for.

Size of sample

Further detailed study of results of routine indicator crop readings on certain nematode control experiments in Hawaii disclosed other significant information on the accuracy of the indicator plant as a measure of soil infestation. In a 20-acre field undergoing fallow treatment, cowpeas were planted in September 1931 as indicators in 20 uniformly spaced blocks, 5 blocks lengthwise and 4 crosswise of the field. Each block contained approximately 500 plants in an area of approximately 500 square feet, one plant to each square foot of surface. It was the plan to obtain fairly complete readings on degree of infestation in each block, and then judge as to infestation of the entire field by degree of uniformity of infestation in the blocks, and by gradations in infestation from end to end or from side to side, if such gradations occurred. For purposes of the present discussion each block is considered as a distinct plot.

Granting the usefulness of gall counts as an indication of degree of infestation of the particular soil in which the plant is grown, the question arises as to numbers of plants necessary to get an adequate reading on a large plot or field area under observation. This problem was studied in the present instance by plotting the readings in average number of galls per plant obtained on various groups of plants of gradually increasing magnitude, selected at random from each of the 20 plots, until an adequately close parallelism of curves was obtained. This was done for the first 10 plants, the first 25, the first 50, and the first 100, and then for 400 as sufficient to represent the entire block. The results are shown in figure 1. It is to be seen at a glance that the lines are fairly close together, so close in fact that many of them are obscured as individual lines. One is led to the conclusion that, for rough readings at least, as few as 10 plants, or certainly 25, are sufficient to give a general idea as to the

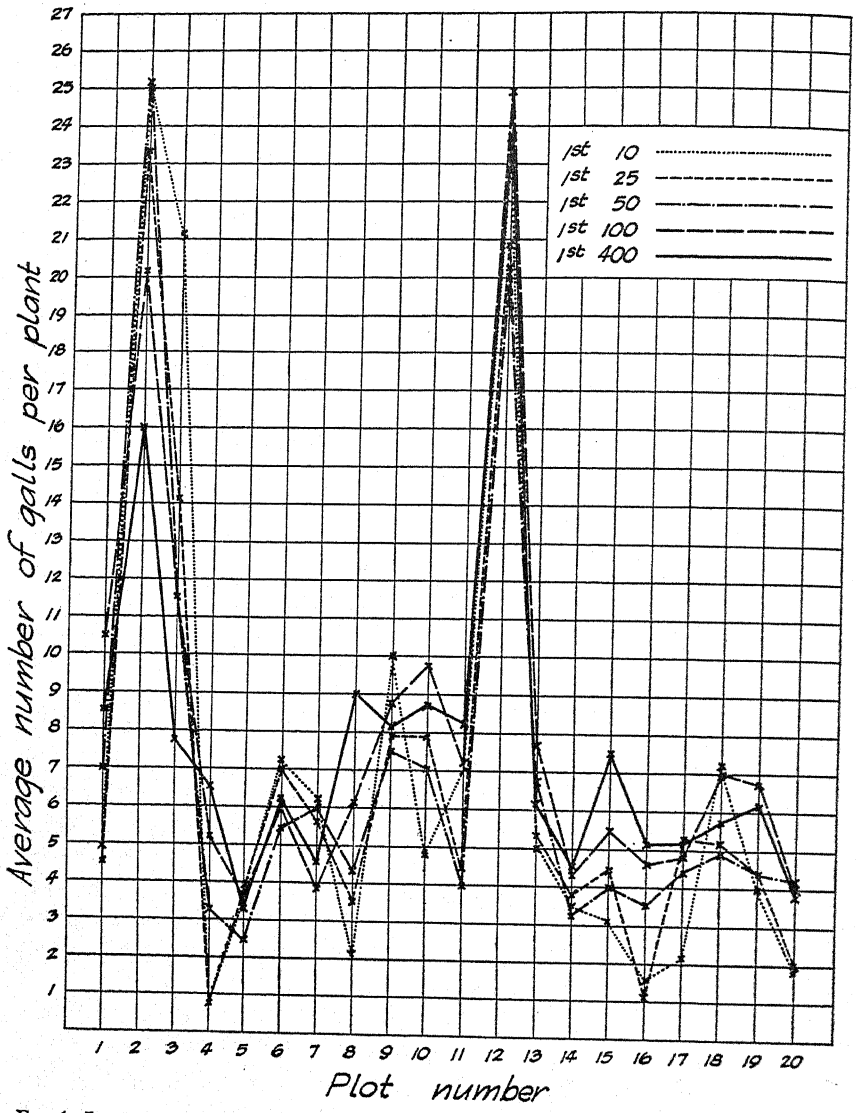


FIG. 1. INDICATOR CROP READINGS IN AVERAGE NUMBER OF GALLS PER PLANT ON 20 DIFFERENT PLOTS, WITH 10, 25, 50, 100, AND 400 PLANT READINGS ON EACH PLOT

Note the good parallelism throughout. The two high points are consistently the high ones for all readings; the low ones for the 400-plant readings (plots 5, 7, 14, 16, 17, and 20) show relatively low readings for all the lower plant numbers; intermediate points are likewise fairly consistent. Readings on 25, 50, or 100 plants in a block may as a rule be taken as representative of the entire block.

distribution of infestation in the field. The two plots that are distinctly high, numbers 2 and 12, are manifestly the highest for all the lines shown. Likewise the low points, plots 5, 16, and 20 are uniformly low for all readings. The remainder of the plots are fairly uniform in degree of infestation, and all readings alike indicate this; such differences as are shown are not particularly important in so far as the main objective is concerned. It is obvious that discrepancies are present, however. A comparison of the 100-plant readings, for example, with the entire-plot readings, shows that whereas in most plots the average of the 400 group is intermediately placed, in certain plots it is distinctly above or below. In plot 2, for example, with a reading of 20 galls for the first 100, the reading for 400 is 16, which means that some of the other 100-plant readings must be distinctly lower yet. Had another 100 been taken instead of the first, a somewhat different picture would have been obtained for this plot. Even then, however, a relatively high position would have been retained, as will be shown if the position 13.25 (the lowest reading of a lot of 100) is plotted. Thus the picture would not have been greatly distorted at its worst. The significant point is that even a 20 per cent error from this method will not give an entirely wrong conception, where really important and significant differences between plots occur. As a rule such significant differences in nematode infestation brought about by any kind of treatment whatever, are on the order of 10 to 1 or greater. This is discussed in greater detail elsewhere in this paper.

When the same data as those from which this graph was constructed were used, the relatively close parallelism of the curves was manifested mathematically by a study of correlations. The self-correlation of the first 20 plants was determined, by calculating the correlation of the first 10 with the second 10, as .773 $\pm$.06. The self-correlation of the first 50 was .831 $\pm$.04. That of the first 100 was .845 $\pm$.04. That of the first 200 was .73 $\pm$.06. This latter figure is low again, in confirmation of the conclusion drawn from figure 1. The correlation of the first 100 with the first 400 plants, however, is .903 $\pm$.03, which is highly significant of the fair degree of accuracy of a reading on 100 plants only, instead of on 400 or more.

Correlation between gall count and per cent of plants infected

A still further study of the data from the 20 plots under consideration disclosed a high correlation between readings on percentage of plants infected and average number of galls per plant, particularly if a fairly large number of plants is considered. The data were taken from 80 lots of 100 plants each (4 lots from each of the 20 plots), and a correlation table was prepared, per cent plants infected against average number of galls per plant (fig. 3). The correlation (r) is .73 $\pm$.035. It is evident, however, that there is not a straight line relationship, but rather a curved line relationship. The non-linear correlation, *eta*, based on the same dates, was found to be .948 $\pm$.013, which is remarkably high. This can be interpreted as indicating that it would be better,

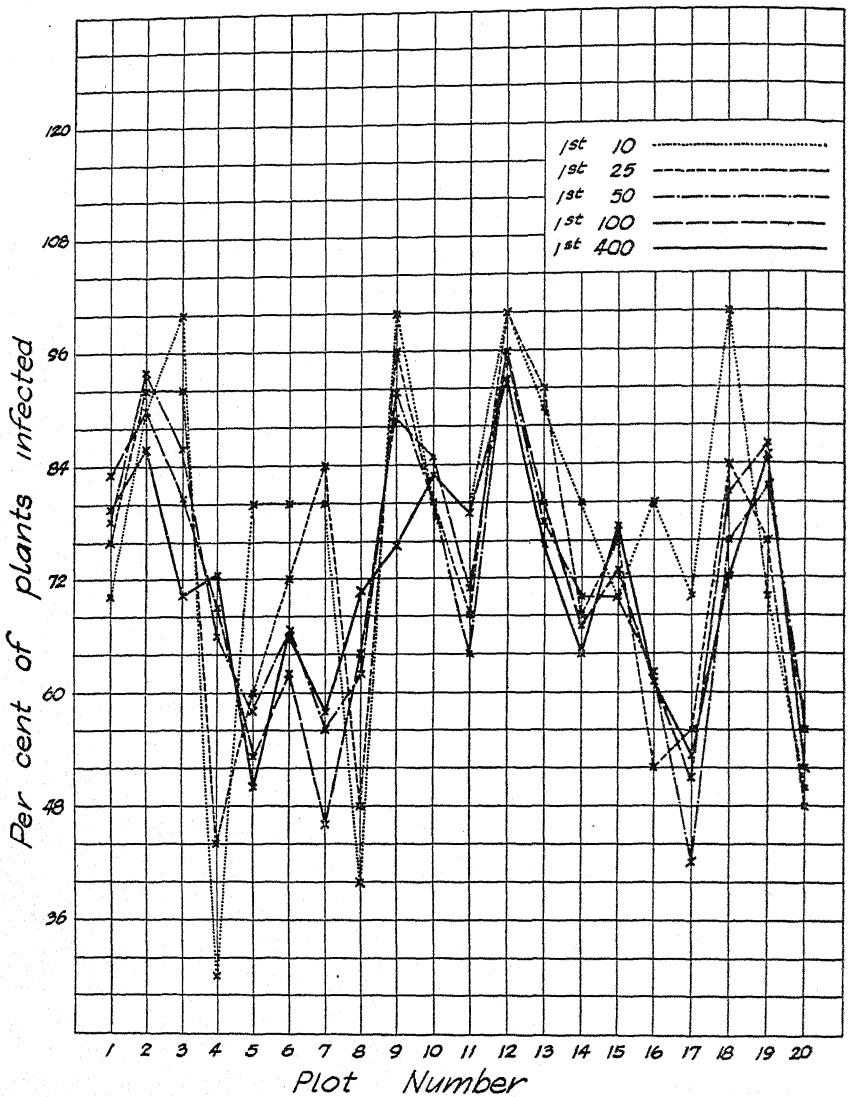


FIG. 2. INDICATOR PLANT READINGS ON THE SAME PLOTS AS IN FIGURE 1, IN PERCENTAGE OF PLANTS SHOWING INFECTION, ON THE SAME 25 TO 400 PLANTS PER PLOT

Note the close parallelism throughout at least the higher plant numbers. Note also the correspondence in high and low points between this graph and figure 1, showing that for infestations that show not more than about 30 galls average per plant, percentage infection counts alone are almost as satisfactory as actual gall counts. See figure 3 for the correlation between the two.

instead of actually counting numbers of galls, to classify the indicator plants only as infected and free, which can be done very quickly after the roots are thoroughly washed.

To study this point still further, the data on per cent of plants infected were plotted, similarly to figure 1, on the first 10, 25, 50, 100, and 400 plants as representative of the whole. The curves obtained (fig. 2) are very similar to those shown in figure 1 in displaying a high degree of parallelism. The low count averages show consistently greater variability, the averages for the

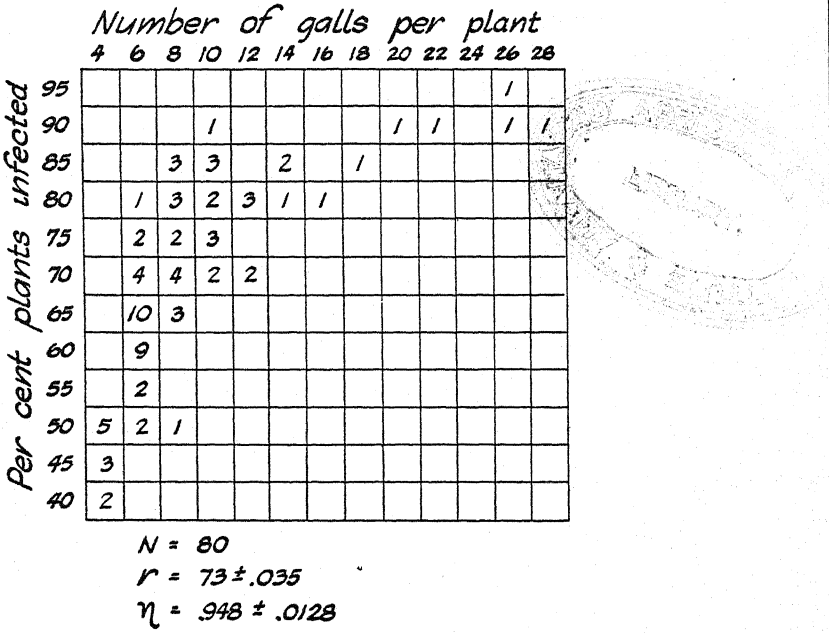


FIG. 3. SCATTER DIAGRAM, FOR CORRELATION CALCULATIONS, SHOWING THE CURVED-LINE CORRELATION BETWEEN GALL-COUNT READINGS AND PERCENTAGE-INFECTION READINGS ON 80 SEPARATE LOTS OF 100 PLANTS EACH, WHERE GALL COUNT RANGES BETWEEN 0 AND 30 PER PLANT.

higher number groups tending to bring the whole series more nearly to a level. It is obvious, too, from a comparison of figure 1 with figure 2, that the high points in figure 2 (plots 2 and 12, 400 group averages) are the same as those for figure 1. The greater height in figure 1 is consistent with the curved line relationship shown by the correlation table (fig. 3). Likewise the low points, plots 5, 7, 14, 16, 17, and 20 are identical in the two. In brief, it is evident that the same sort of relationship in degree of infestation in the different plots could have been established by a mere classification of plants as infected or non-infected, instead of by the more laborious gall-count method. The time and labor saved by the simpler classification are tremendous.

With the complete data at hand, it was a simple matter to study mathematically the relative reliabilities of the different number-groups on which records were kept. The data upon which this study is made are given in table 2. The self-correlation of the first 20 plants, as to percentages infected, determined by correlating the first 10 with the second 10, was .406 ±.127; of the first 50, .482 ±.116; of the first 100, .726 ±.06; of the first 200, .913 ±.02. It is evident that reliability increases with increase of numbers, as is, of course, to be expected. The correlation of per cent of infested plants in the first 100 with that of the entire 400 is .91 ±.028, which is fairly high, and indicates

TABLE 2

Record of per cent of plants infected from a series of 20 plots

BLOCK	1ST 10	2ND 10	1ST 20	1ST 25	2ND 25	1ST 50	2ND 50	1ST 100	2ND 100	1ST 200	1ST 400
1	70	80	75	76	80	78	88	83	76	79.5	78.5
2	90	90	90	92	96	94	86	90	84	87	85.75
3	100	90	95	92	80	86	78	81	81	81	71
4	30	80	55	44	88	66	72	69	78	73.5	73
5	80	50	65	60	56	58	48	53	49	51	50
6	80	70	75	72	60	66	58	62	63	62.5	65.5
7	80	80	80	84	28	56	36	46	42	44	57.75
8	40	60	50	48	76	62	66	64	73	68.5	70.5
9	100	100	100	96	88	92	86	89	86	87.5	75.75
10	80	80	80	80	80	80	90	85	90	87.5	83
11	80	50	65	68	60	64	78	71	87	79	79
12	100	100	100	100	92	96	96	96	93	94.5	93
13	90	90	90	92	64	78	82	80	81	80.5	75.5
14	80	60	70	68	72	70	64	67	69	68	64
15	70	90	80	76	64	70	76	73	74	73.5	77.5
16	80	40	60	52	72	62	60	61	62	61.5	61.25
17	70	50	60	56	28	42	60	51	55	53	53.25
18	100	60	80	84	68	76	86	81	73	77	72
19	70	70	70	76	88	82	84	86	86	86	85.25
20	50	40	45	48	64	56	48	52	54	53	51.75

that for most purposes this sort of reading on 100 plants is sufficient in comparing different plots in which high differences are to be expected. When one has decided to make comparisons between plots on the basis of percentage of indicator plants infected, an increase in numbers of plants for the sake of increased reliability is not so serious a matter as it would be if gall counts were to be made, because of the great difference in time required for examination.

In practice, the translation of readings in terms of percentage of indicator plants infected over to number of galls per plant and thence to populations per acre is practicable only if based upon a curve prepared from a large number of data—much larger than those included in figure 3—and then over only a limited range. It is evident from figure 3 that percentage readings in the

neighborhood of 100 might be taken on areas whose gall count would be anywhere from 30 up, indicating populations anywhere above about 180 nematodes per cubic foot. On the other hand, readings below this point are distinctly low, as nematode populations go, and clearly indicate absence of the heavy infestations that are frequently encountered. For such readings a rough indication of a curve in figure 3 might be useful for approximations. If low populations are actually uniformly distributed through the soil, 100 per cent infection of indicator plants might occur, and figure 3 would be entirely misleading.

The factor of time in estimating nematode populations

Often the time available for making counts is a governing factor in the criterion to be used. Records were maintained on the amount of time expended on the operations, in connection with some of the data reported in the foregoing sections. In one lot of several thousand plants in which gall counts varied from 0 to 60 per plant, the time consumed by an average laboratory assistant averaged approximately 1 minute per plant. In examinations in which presence or absence of infection alone is being recorded, detailed examination is necessary only on plants that have very low or zero gall counts, for it is important that complete freedom be established definitely. In one such lot between 4 and 5 were examined per minute, or better than 2,000 in a single day. Labor of removing plants fairly carefully from the soil was at the rate of approximately 1,000 plants per day. Thus for the presence or absence criterion the time consumption is less than 2 days for a thousand plants. In other words satisfactory nematode population estimates were made on a "sample" of 1,000 separate square-foot areas in a field in less than 2 days. Where galls must be counted, of course, the time requirement is more nearly 4 days, more if gall counts are high. It must be considered, of course, that by the indicator crop method a delay of at least a month, for the growth of the plants, is necessary before the report can be made.

DISCUSSION

The usefulness of the indicator crop method of making nematode population estimates has been repeatedly demonstrated at this station. Data from many experiments have been assembled, showing results similar to those herein reported. In the Johnson and Godfrey (23) paper on chloropicrin for nematode control, examination of the charts shows at a glance the parallelism between readings on the basis of freedom from infection and those on numbers of galls. In another soil fumigation experiment recently reported (12) the reliability of the indicator crop readings as an indication of extent of control obtained, is demonstrated. A correlation for 49 plots, of $-.852 \pm .0265$ was shown between an early, roughly made indicator plant reading and crop yield.

It is in such experiments as these, in which wide variations between plots are to be expected and plantings are made all at one time, that the method has

been found to be particularly reliable. Where studies have been made to show seasonal variations in nematode infestation in the same field, with readings taken at wide intervals, discrepancies have occurred that are not yet fully understood. For example, in one field a fall reading was higher than the one taken the previous spring, without opportunity for an increase to have occurred in the interim. Undoubtedly some environmental factor influenced the amount of infection that occurred. For such studies, due consideration must be given to the differences in environmental conditions.

Several years of experience in observing root-knot nematode infestation in pineapple fields in Hawaii have led to the conclusion that, in a field undergoing treatments for nematode reduction, survival of infestation is likely to be irregular, some spots showing definite survival and others being entirely free. Likewise for any particular infested area nematode populations are likely to change rather rapidly. In the absence of a susceptible host plant of any kind it is gradually but constantly diminishing, due to natural enemies, to unfavorable factors of the immediate environment, or to actual starvation. On the other hand reproduction in a single spot on a susceptible weed or volunteer crop plant will bring about a rapid rise of population. These irregularities contribute to spotted infestations in a field. Any rate whatever of survival will, after the planting of a susceptible crop, eventuate after sufficient time in the building-up of a high population. High efficiency of a treatment for nematode control is likely to mean a high percentage of the area free from nematodes, rather than reduction to a uniform low population throughout.

From this point of view, in an attempt to measure the soil infestation at any given time, any means that measures the percentage of area relatively free from infestation is highly useful. The indicator crop method has shown itself to be particularly good for this purpose. Such a crop is seeded in several different areas in the field (at least 20 if the field is a large one) in blocks of 25, 50, or 100, spaced about a foot apart. If the percentage of plants showing infection at the end of a single life cycle of the nematode (30 days, more or less depending upon temperature) is high, approaching 100 per cent, then, as has been shown in this paper (fig. 3) the average number of galls per plant will be high and the soil population can be considered to correspond. At least a 30-gall count per plant will be indicated, and this means (see table 1) a population of not less than 150 per cubic foot and the possibility of a very much greater one. If the condition of the indicator crop roots indicates a much higher gall count than 30, then actual gall counts may be made if it seems desirable, and on the basis of the average obtained the actual magnitude of the infestation may be estimated.

A number of circumstances necessitate special factors with which to multiply the reading, where soil populations are distinctly high. When the gall count on a cowpea indicator plant is 1,000 or higher, as is frequently the case, the root system is greatly reduced and therefore does not detect infestation beyond its limited range. The range of a root system with 1,000 to 2,000 galls is

about 350 cubic inches or 1/5 cubic foot. Multiplying such gall count by the factor 5, then, would give an estimate of the gall count to be expected had the root system penetrated the entire cubic foot. Multiplying this again by about 4 (see table 1) would give an estimate of the average cubic foot population. Slightly lower gall counts would call for a lower factor than 5 and higher gall counts for a higher factor, to provide for differences in root growth.

The alternative is suggested of removing indicator plants from the soil with the aid of a firm metal cylinder of appropriate size thrust into the soil surrounding the plant to a chosen depth, and then lifting the plant, soil and all, with the aid of an appropriate tool. The roots could then be carefully freed from soil, and gall counts could be made. Such a cylinder exactly 8 inches deep and 7.42 inches in diameter would lift exactly 1/5 cubic foot of soil. The factor 5, then, could be used for all plants alike to estimate the possible gall count for the entire cubic foot. If infestation were so heavy and roots so reduced that no roots were cut by the cylinder, the population estimate would merely state "over (the calculated amount)."

Returning to the consideration of the percentage of indicator plants merely showing the presence of infection, we see from figure 3 that if this percentage is low, the average amount of infection per plant will be low, and the nematode population per cubic foot or per acre-foot, correspondingly low. Furthermore there will be a high percentage of plants that will at least start growth free from infection and thus establish a good root system. They will remain free until the relatively low number of nematodes that escaped detection, deep in the soil, perhaps, becomes effective, or until spread occurs from nearby spots that may have been more heavily infested. For annual crops, such light initial infestations are likely to be of minor importance because of the shortness of the growing season, except that they serve to spread and increase the nematode population and thus to make the problem of control a more serious one for the subsequent season.

In choosing between gall count method and the method of recording only percentages of plants infected, the investigator is governed by the need for accuracy, the nature of the information desired, and the cost consideration. The gall count method is undoubtedly the more accurate of the two. Where really efficient control measures are undergoing test, where differences on the order of 10 or more to 1 are to be expected, the percentage count as a rule gives a fair indication of results obtained. Gall counts will probably be necessary for an adequate quantitative comparison. If plot differences are not expected to be great, as for instance between two series with different quantity applications of a soil fumigant, increased accuracy of comparisons will be obtained with increased numbers of indicator plants by either method. Other things being equal, the time and labor elements as factors in the choice of method, point definitely toward the percentage count as much the more economical.

It is evident that the time consumed by the indicator crop method of root-knot nematode population estimation is only a small fraction of that required

for the direct soil census method, for comparable samplings. Readings on at least 500 separate spots in a field can be made by means of indicator crops in the time required for a single really adequate soil sample reading. The same statistical laws apply to increase in accuracy with increase in numbers of samples, and to advantages from composite samples, in both cases. The indicator crop has proved, as well, to be even more accurate than the other method in detecting small populations and in estimates of the populations based upon such findings. It would be virtually impossible, short of days of intensive laboratory search, to be certain of finding a single larva in a 400-cc. sample of muddy soil, which is equivalent to 80 larvae in a cubic foot. Table 1 in this paper shows that not only was this population detected, but the count was fairly uniform in 20 such samples, thus justifying the use of such a count as a basis for estimating the total population. Furthermore, nematodes present in the form of scattered eggs, which of course are very small (88 x 55μ) and almost certain to be missed by the direct count method, will have an abundant opportunity to hatch and thus to be caught by the plant during the month of exposure to infection. Baunacke (1) states that, with the similar organism, *H. schachtii*, the mere presence of the susceptible plant stimulates to hatching eggs that would otherwise lie dormant. The same may be true for *H. marioni*, though it has not been proved.

It is important, of course, that in field exposures, indicator crops be planted only under conditions favorable for plant growth and for nematode activity. If it becomes necessary to take readings at a season unfavorable in either respect, then composite samples from the field can be collected, thoroughly mixed, and aliquot portions taken to the greenhouse for plantings in pots. This increases the cost in labor and time. It likewise decreases the accuracy somewhat, for any errors made in counts are multiplied by the proportion of the aliquot to the entire sample. The fact that such samples are in closed containers, however, makes for greater certainty of a high percentage of "catch," so that calculations of plot populations based upon gall counts therein are actually highly reliable. The soil sampling phase of the indicator crop method, therefore, likewise has an important field of usefulness.

A criticism of the indicator crop method may be directed toward the host preference or biological strain conception. Steiner (31) has pointed out that with the root-knot nematode such host preference may play an important part in the amount of infection that may occur in a new planting. Goodey (19) has recently discussed the biological strain situation with various plant parasitic nematodes. He does not include *H. marioni* specifically in his major discussion. In the writer's experience with this organism, one of its striking characteristics is its ready adaptability to a wide range of families of host plants. While with the U. S. Department of Agriculture he (11) used nematodes originating on a weed *Urena lobata* L. on uncultivated land, for successful inoculations of tomato, tobacco, cowpea, soybean, potato, cucumber, and vetch. More recently Godfrey and Oliveira (16) and Collins and Hagan

(5) have used egg masses obtained from cowpeas to produce heavy infections in pineapple (*Ananas comosus* [Linn.] Merr.). The reverse inoculation is made frequently in the course of various phases of the work at this station. Commercial greenhouse experience everywhere shows that successions of nematode susceptible plants such as cucumbers and tomatoes are heavily damaged in turn when planted in the same nematode infested soil. This does not argue against the existence of host strains, for there may be a mixture of such strains present. Detailed carefully controlled experiments with families of known history should be performed to establish the existence or non-existence of clearly defined host strains of *Heterodera marioni*. If their existence becomes established, then, for indicator crop purposes, a judicious choice of plant suited to the particular strain under observation may be demanded.

SUMMARY

The indicator crop method for the study of degree of soil infestation with the root-knot nematode, *Heterodera marioni*, consists of planting a highly susceptible plant such as English pea (*Pisum sativum* L.), cowpea (*Vigna sinensis* L. Endl.), or tomato (*Lycopersicon esculentum* L.) in the soil to be tested, under favorable conditions for growth and for infection, and, after the expiration of sufficient time for the completion of the first life cycle but not for the initiation of the second (averaging about 30 days), removing the plants and making detailed records of degree of infection. These records may be in terms of numbers of galls per plant, or, with low initial infestation, in terms of percentage of indicator plants infected. Statistical studies on a large number of plants showed a high correlation between gall count on roots and actual numbers of contained nematodes, thus enabling the investigator to estimate, on the basis of gall count alone, total numbers of nematodes caught in the roots. Other studies showed additional high correlations, given in the body of the paper, from which were derived regression formulas with which, on the same basis of gall counts, fairly accurate estimates could be made of the total nematode population of the soil on the cubic foot or acre foot basis. With relatively low counts of 30 galls or less average per indicator plant root, the very much less time-consuming task of count of percentage of plants infected was found to be a fairly accurate measure of degree of soil infestation, since the correlation was found to be very high between percentages of infected plants ranging from 1 to 100, and actual gall counts ranging from 1 to 30, average, per plant. Observations on from 25 to 100 indicator plants per block are sufficient, the accuracy of estimates being greater of course, with the larger numbers. It is considered desirable to have at least 20 such separate blocks of plantings in a large field. With increased knowledge for different crops and climatic conditions, already obtained in part for pineapples in Hawaii, as to the potentialities for damage of known degrees of soil infestation, the value of the knowledge obtained from the application of this method is very evident. Gall count or percentage count readings can be transformed to

estimates of actual soil populations with a fair degree of accuracy, by application of derived factors and regression formulas, where such estimates are considered desirable. Such factors and formulas, as given in the body of this paper, require study and judicious appraisal before they are applied extensively. Further extensive refinement of this phase of the study is called for, with ultimate development of factors and formulas based upon a large number of actual cases and conditions. It is believed, however, that the basic method here presented is a sound one and that in accuracy as well as in simplicity of application it is superior to a direct soil census. It may be used as it stands, with gall counts alone, for plot or field comparisons, with assurance of reasonable reliability. Errors of 20 or 25 per cent often do not alter major conclusions.

REFERENCES

(1) BAUNACKE, W. 1922 Untersuchungen zur Biologie und Bekämpfung des Rübennematoden *Heterodera schachtii* Schmidt. *Arb. Biol. Reichsanst. Land u. Forstw.* 11: 1850288.

(2) BUCKHURST, A. S., AND FRYER, J. C. F. 1931 The problem of "potato sickness." A report upon certain experiments. *Ann. Appl. Biol.* 18: 584–901.

(3) BYARS, L. P. 1919 Experiments on the control of the root-knot nematode, *Heterodera radicicola* (Greef) Müller. I. The use of hydrocyanic-acid gas in loam soil in the field. *Phytopath.* 9: 93–103.

(4) COBB, N. A. 1918 Estimating the nema population of soil. U. S. Dept. Agr. Bur. Plant Indus. Agr. Technol. Cir. 1.

(5) COLLINS, J. L., AND HAGAN, H. R. 1932 Nematode resistance of pineapples. Varietal resistance of pineapple roots to the nematode *Heterodera radicicola* (Greef) Müller. *Jour. Heredity* 23: 459–465; 503–511.

(6) CONRAD, JOHN P., AND VEIHMEYER, F. J. 1929 Root development and soil moisture. *Hilgardia* 4: 113–134.

(7) DEONG, E. R., AND TYLER, JOCELYN 1928 Potassium xanthate as a soil fumigant: II. *Indus. and Engin. Chem.* 20: 912–916.

(8) GARRETT, HENRY E. 1931 Statistics in Psychology and Education. Longmans, Green and Co.

(9) GODFREY, G. H. 1923 Root-knot: its cause and control. U. S. Dept. Agr. Farmers' Bul. 1345.

(10) GODFREY, G. H. 1924 The depth distribution of the root-knot nematode, *Heterodera radicicola*, in Florida soils. *Jour. Agr. Res.* 29: 93–98.

(11) GODFREY, G. H. 1926 Effect of temperature and moisture on nematode root-knot. *Jour. Agr. Res.* 33: 223–254.

(12) GODFREY, G. H. *In press.* Experiments on the control of the root-knot nematode in the field with chloropicrin and other chemicals. *Phytopath.*

(13) GODFREY, G. H., AND HAGAN, H. R. 1933 Influence of soil hydrogen-ion concentrations on infection by *Heterodera radicicola* (Greeff) Müller. *Soil Sci.* 35: 175–184.

(14) GODFREY, G. H., AND HOSHINO, HELENE M. 1932 Studies on certain environmental relations of the root-knot nematode *Heterodera radicicola*. *Phytopath.* 23: 41–62.

(15) GODFREY, G. H., AND HOSHINO, HELENE M. *In press.* The trap-crop as a means of reducing root-knot nematode infestation. *Phytopath.*

(16) GODFREY, G. H., AND OLIVEIRA, JULIETTE 1932 The development of the root-knot nematode in relation to root tissues of pineapple and cowpea. *Phytopath.* 22: 325–348.

(17) GODFREY, G. H., OLIVEIRA, JULIETTE M., AND GITTEL, ERNA B. H. 1933 The duration of life of the root-knot nematode, *Heterodera radicicola*, in soils subjected to drying. *Soil Sci.* 35: 185–195.

(18) GOFFART, H. 1932 Untersuchungen am Hafernematoden *Heterodera schachtii* Schm. III. Beitrag zu: Rassenstudien an *Heterodera schachtii* Schm. *Arb. Biol. Reichsanst. Land -u. Forstw.* 20: 1–26.

(19) GOODEY, T. 1931 Biological races in nematodes and their significance in evolution. *Ann. Appl. Biol.* 18: 414–419.

(20) GUBA, E. F. 1932 Carbon disulphide emulsion for the control of the root-knot nematode. Mass. Agr. Exp. Sta. Bul. 292.

(21) HODSON, W. E. H., AND GIBSON, GORDON W. 1928 Some experiments with calcium cyanide as a control for plant parasitic nematodes. *Ann. Appl. Biol.* 15: 639–648.

(22) HOSHINO, HELENE M., AND GODFREY, G. H. 1933 Thermal death point of *Heterodera radicicola* in relation to time. *Phytopath.* 23: 260–270.

(23) JOHNSON, M. O., AND GODFREY, G. H. 1932 Chloropicrin for nematode control. *Indus. and Engin. Chem.* 24: 311–313.

(24) JONES, LINUS H. 1932 The effect of environment on the nematode of the tomato gall. *Jour. Agr. Res.* 44: 275–285.

(25) MCCLINTOCK, J. A. 1930 Testing soils for nematode content. Tenn. Agr. Exp. Sta. 42d. Ann. Rpt. 1929: 37.

(26) MORGAN, D. O. 1925 Investigations on eelworm in potatoes in South Lincolnshire. *Jour. Helminthol.* 3: 185–192.

(27) NEWHALL, A. G. 1930 Control of root-knot nematode in greenhouses. Ohio Agr. Exp. Sta. Bul. 451.

(28) SMITH, A. M. 1929 Investigations on *Heterodera schachtii* in Lancashire and Cheshire. Part II. The relationships between degree of infestation and hygroscopic moisture, loss on ignition, and pH value of the soil. *Ann. Appl. Biol.* 16: 340–346.

(29) SMITH, A. M., AND MILES, HERBERT W. 1929 Investigations on *Heterodera schachtii* in Lancashire and Cheshire. Part III. Certain correlations between crop yields and degree of infestation. *Ann. Appl. Biol.* 16: 596–601.

(30) SMITH, A. M., AND PRENTICE, E. G. 1929 Investigations on *Heterodera schachtii* in Lancashire and Cheshire. Part I. The infestation in certain areas as revealed by cyst counts: an estimation of the errors involved in the technique and a correlation with intensity of disease. *Ann. Appl. Biol.* 16: 324–339.

(31) STEINER, G. 1925 The problem of host selection and host specialization of certain plant infesting nemas and its application in the study of nemic pests. *Phytopath.* 15: 499–534.

(32) THORNE, GERALD 1922 The sugar-beet nematode in the western states. U. S. Dept. Agr. Farmers' Bul. 1248.

(33) THORNE, GERALD 1923 Length of the dormancy period of the sugar-beet nematode in Utah. U. S. Dept. Agr. Dept. Cir. 262.

(34) TRIFFITT, MARJORIE J. 1929 Preliminary researches on mustard as a factor inhibiting cyst formation in *Heterodera schachtii*. *Jour. Helminthol* 7: 81–92.

(35) TRIFFITT, MARJORIE J. 1929 Observations on the incidence of *Heterodera schachtii* at the Ormskirk potato testing station. *Jour. Helminthol* 7: 93–98.

(36) TYLER, JOCELYN 1933 Development of the root-knot nematode as affected by temperature. *Hilgardia* 7: 391–415.

(37) WATSON, J. R. 1917 Control of root-knot by calcium cyanide. Fla. Agr. Exp. Sta. Bul. 136.

(38) WATSON, J. R. 1922 Bunch velvet beans to control root-knot. Fla. Agr. Exp. Sta. Bul. 163.

A NEW METHOD OF MEASURING THE AQUEOUS VAPOR PRESSURE OF SOILS

N. E. EDLEFSEN

University of California

Received for publication August 16, 1933

Practically all soil characteristics with which engineers or agricultural investigators are concerned are related in some way to the force (4) with which water is held in the soil at various moisture contents. These characteristics may be the capacity of the soil to support different loads, the condition of tilth, ability to hold water, availability of water to plants, ability to resist erosion, or permeability to water. The force is related to a number of colligative properties of soil moisture. In an investigation of soil moisture conditions, a method for studying the thermodynamic properties over the entire range of moisture content is needed. Some methods prove satisfactory for wet soils whereas others work better for dry ones. After considering the other methods, the writer decided that a vapor pressure method offered the best possibilities for studying the soil moisture over its entire range.

Several investigators (8, 9, 10, 12, 13, 17) have discussed the various methods of measuring vapor pressure of soils; and Thomas in particular has pointed out the value of this function in throwing light on the various soil-moisture phenomena. His article contains a rather complete survey of the work accomplished in this field, together with a complete bibliography, and also summarizes the theoretical relations connecting vapor pressure with other colligative properties of water in soils. Somewhat more definitely than other investigators, he has pointed out two main objections to vapor pressure methods; namely, the length of time required for making single determinations by the static method and the work involved in case of the dynamic method. The idea of overcoming some of these difficulties, if possible, led to the present investigation.

DESCRIPTION OF METHOD

As noted, one objection to the static method is the length of time required to obtain equilibrium. This difficulty is materially increased when air is present. If, however, a high vacuum is obtained, the time required for attaining equilibrium is comparatively short. In recent studies on the aqueous vapor pressure of water in soils, the writer (5) developed a special method that proved very satisfactory from the standpoint of accuracy and speed. The apparatus is shown in figure 1.

The method consisted of putting a sample of about 4 gm. of dry soil on the

pan, C, supported on a sensitive calibrated Jolly balance spring, F. This balancing arrangement served both as a weighing device and as an indicator of equilibrium. The sample was usually wet first and then allowed to dry in air. Next, it was suspended from the spring; and the cup, B, was placed over it and sealed at the ground glass joint, A, with stopcock grease. This glass

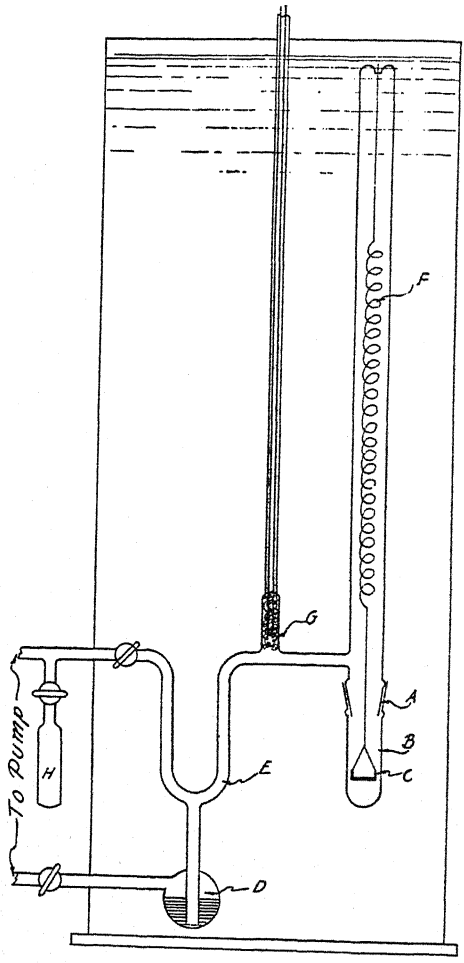


FIG. 1. ARRANGEMENT OF APPARATUS USED FOR MEASURING VAPOR PRESSURE OF SOILS

system was air tight; and after the cup was sealed in place, the gases were exhausted through the U-tube, E, until a pressure of not more than 10^{-5} mm. of mercury existed. This pressure was found not to increase materially over considerable periods of time after the exhaustion had been carried on for a few hours. After the system had been evacuated, air-free water vapor was allowed to pass from the vessel, H, through the stopcock to the rest of the system.

This vapor condensed on the soil, wetting it to the desired amount. The procedure was to wet the soil and then dry it by pumping out water vapor, progressively measuring the equilibrium vapor pressure each time. At each step after the desired quantity of water vapor in the system had been obtained, mercury was allowed to rise in the U-tube, E, by increasing the pressure in the vessel, D. This U-tube served as a valve to close off the system from the pump as well as an approximate means of indicating the pressure, since the pressure on the pump side of the U-tube could be reduced very nearly to zero and since the pressures of gases in the chamber other than water vapor were very small. The difference between the two levels gave the approximate pressure of the vapor in the soil chamber.

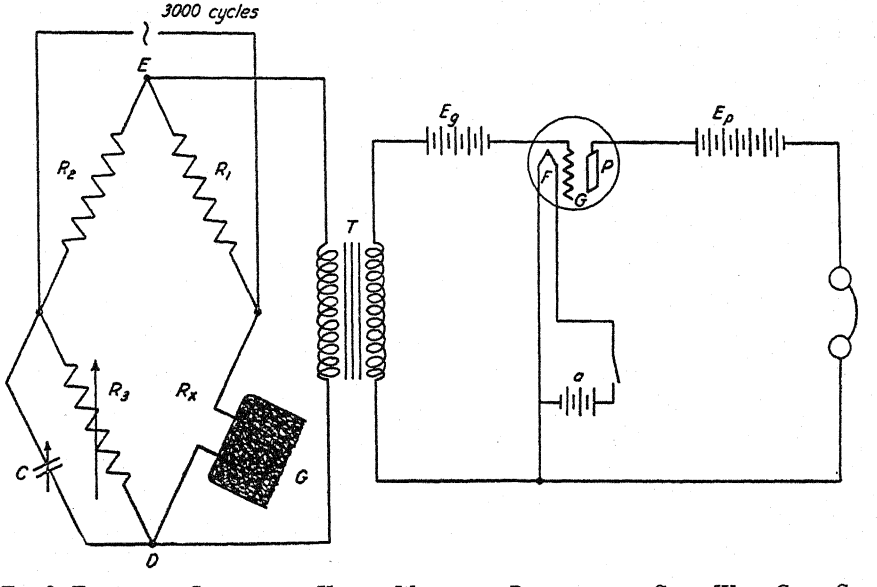


FIG. 2. ELECTRICAL CONNECTIONS USED IN MEASURING RESISTANCE OF GLASS WOOL CELL, G

A glass cell, G, loosely packed with glass wool through which two electrodes extended, was sealed to the chamber containing the soil. The electrical resistance of this cell at a given temperature depends upon the amount of soluble salts remaining on the surface of the fibers, which is constant, and upon the amount of water condensed there, which varies with the vapor pressure. The glass wool was washed in ordinary tap water when the cell was made. All work was done at 30°C.

The electrical connections are shown in figure 2. To avoid polarization, an alternating current of 3,000 cycles per second was used. With one stage of amplification across the bridge, a variation of one ohm in 10,000 could easily be detected. The glass wool cell had an appreciable capacity that varied with the vapor pressure in the chamber. This capacity, of course, had to be bal-

anced by means of the variable condenser, C, before a null could be reached. The resistance of the cell at equilibrium in saturated vapor at 30°C. was about 10,000 ohms and increased to infinity as the vapor pressure decreased to zero.

In calibrating the device, resistance readings were plotted against known vapor pressures. Vapor pressure for calibration was regulated by introducing sulfuric acid solutions of known concentrations into the chamber. First the solution was frozen with liquid air, then the chamber was evacuated to remove all gases, and finally the solution was melted. This procedure lessened the length of time required to reach equilibrium. The solution was stirred from the outside with a magnetic stirrer, and the concentration was determined after the resistance of the glass wool cell was measured. This procedure accounted for the slight amount of evaporation that took place when the solution was introduced into the chamber. Gases were removed, as explained previously, before any vapor was allowed to enter the system. The cell then came to equilibrium in a few hours. The equilibrium moisture content, as indicated by the weight of moist soil, was reached soon after the conductance of the cell, G, reached a constant value. A change in vapor pressure of 0.01 mm. of mercury could easily be measured by this method.

The calibration of the glass wool cell has remained constant over a period of about 9 months.

RESULTS

Some results of vapor pressure measurements on each of two soils and on a half-and-half mixture of the same two soils are shown in figure 3. Curve A represents a vapor-pressure, moisture-content curve for a fine sandy loam; B, the same function for a clay loam soil; C, a half-and-half mixture of these two soils. The heavy vertical lines indicate the permanent wilting percentage (15) as determined by growing sunflowers and the field capacities (16, 3) as measured by the moisture equivalent. From a physical standpoint, it is realized, these quantities are not specific; but they are useful reference values in soil moisture investigations. The horizontal line at the top represents the vapor pressure of the free flat surface of water. Of special interest is the very rapid drop in the vapor pressure depression (that is, the difference between the vapor pressure of water in the soil and the vapor pressure at the free flat water surface) in the neighborhood of the permanent wilting percentage. At this percentage the depression is estimated to be about 0.4 mm. of mercury at 30°C.

In interpreting the meaning of the depression of the vapor at the permanent wilting percentage, it will be helpful to calculate the energy relation existing under such conditions. Consider the system shown in figure 4 and remember that the capillary poential (6, 7, 11) is defined as work done against the capillary field force per unit of mass in moving water from a free flat water surface to the point in question. This quantity is numerically equal to the energy per unit mass required to transfer water from the point in question to a free flat water surface.

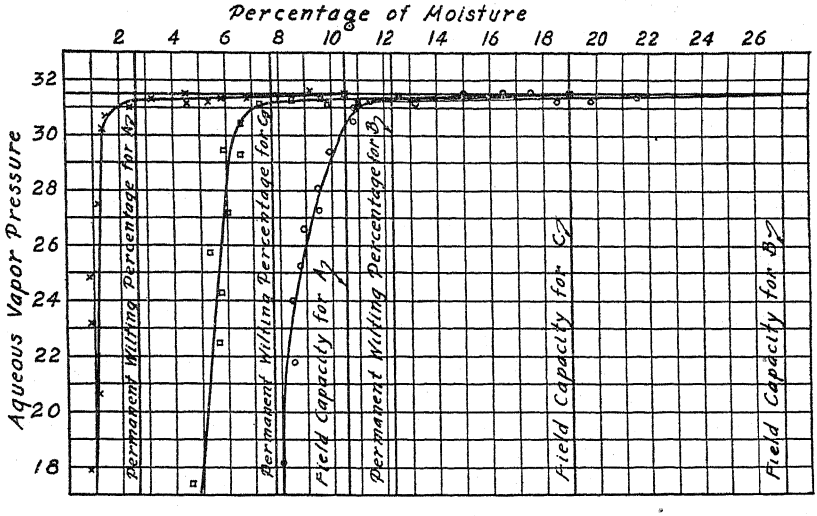
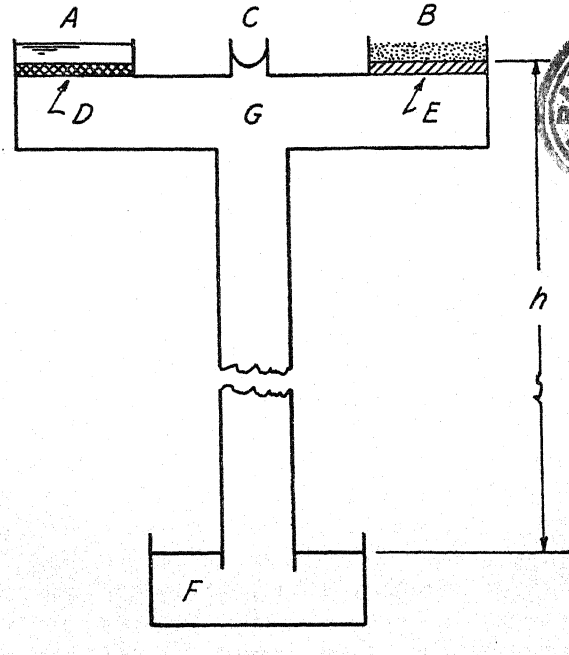


FIG. 3. AQUEOUS VAPOR PRESSURE CURVES, PERMANENT WILTING PERCENTAGES, AND FIELD CAPACITIES FOR A FINE SANDY LOAM, *A*, ON THE LEFT; A CLAY LOAM, *B*, ON THE RIGHT; AND A HALF-AND-HALF MIXTURE, *C*, IN THE CENTER



ALLAHABAD AGRICULTURAL INSTITUTE LIBRARY.

FIG. 4. SYSTEM FOR DEMONSTRATING THE COLLIGATIVE PROPERTIES OF SOIL MOISTURE

A is a chamber having a semipermeable bottom, D, and containing an osmotic solution; B is a chamber having a porous membrane, E, for its bottom and containing soil; C is the top of a capillary tube of height h of appropriate diameter; and F is a vessel of water. The vessel G is filled with water under tension.

With such an isolated system in equilibrium, the following relations hold:

$$p = p_0 e^{-\left(\frac{\rho_0 g h}{p_0}\right)} \tag{A}$$

or, taking the logarithm of both sides and solving for h, we have

$$h = -\frac{p_0 h}{\rho_0 g} ln \frac{p}{p_0} \tag{B}$$

$$\pi = \frac{RT}{V} ln \frac{p_0}{p} \tag{C}$$

$$hgd - p = \pi \tag{D}$$

$$\psi = \phi = -\pi \text{ numerically} \tag{E}$$

$$\phi = \frac{2\sigma}{r} \tag{F}$$

where

e = base of natural logarithm
p = vapor pressure at an altitude h above water level in F
p_0 = vapor pressure at surface of water in F
ρ_0 = density of vapor at surface of water in F
g = gravitational constant
d = density of water
π = osmotic pressure
R = gas constant
T = absolute temperature
V = molal volume of water
ψ = capillary potential
ϕ = pressure of water in the vessel G just under the curved surface of liquid in the capillary tube
h = difference in level between the water in the vessel F and the bottom of the vessels A and B.
σ = surface tension of water
r = radius of curvature of the water surface in C

In the transpiration of water at 30°C. from a saturated soil, 2.42×10^{10} ergs per gram are required. (This is merely the heat of vaporization.) Now, if we add to this the numerical value of the capillary potential at the permanent wilting percentage, we shall have the energy per gram required to transpire water at that moisture content. If we assume the vapor pressure depression at the permanent wilting percentage to be 0.4 mm. of mercury, as the present

measurements indicate, and apply either equation (*B*) or (*C*) and (*E*), we find $\psi = -1.8 \times 10^7$ ergs per gram or $2.42 \times 10^{10} + 1.8 \times 10^7 = 2.4218 \times 10^{10}$ ergs per gram to transpire water at the permanent wilting percentage, which is about 0.7 per cent more than at saturation.

This calculation is interesting because, as pointed out by Veihmeyer, Hendrickson, and others, water is transpired at the same rate, to a first approximation over the entire range of moisture content from permanent wilting percentage to field capacity (1, 2, 14). This result is what might be expected if frictional forces can be neglected. A slight decrease in the moisture content below the permanent wilting percentage produces a large vapor pressure depression and consequently increases by a large amount the energy required to transpire water.

REFERENCES

(1) BECKETT, S. H., BLANEY, H. F., AND TAYLOR, C. A. 1930 Irrigation water requirement studies of citrus and avocado trees in San Diego County, California, 1926 and 1927. Calif. Agr. Exp. Sta. Bul. 489.

(2) BECKETT, S. H., AND DUNSHEE, C. F. 1932 Water requirements of cotton on sandy loam soils in southern San Joaquin Valley. Calif. Agr. Exp. Sta. Bul. 537.

(3) BODMAN, G. B., AND MAHMUD, A. J. 1932 The use of the moisture equivalent in the textural classification of soils. *Soil Sci.* 33: 363–374.

(4) EDLEFSEN, N. E. 1932 Forces acting on soil moisture in relation to other fundamental functions. *Trans. Amer. Geophysical Union:* 1932, 328–330.

(5) EDLEFSEN, N. E. 1933 A glass wool cell for measuring aqueous vapor pressure. *Rev. Sci. Instr.* 4: 345–346.

(6) GARDNER, W. 1920 The capillary potential and its relation to soil-moisture constants. *Soil Sci.* 10: 357–359.

(7) GARDNER, W., ISRAELSEN, O. W., EDLEFSEN, N. E., AND CLYDE, H. S. 1922 The capillary potential function and its relation to irrigation practice. *Phys. Rev.* 20: 196.

(8) KEEN, B. A. 1931 The Physical Properties of the Soil. Longmans, Green and Company, London.

(9) PURI, A. N. 1925 A critical study of the hygroscopic coefficient of soil. *Jour. Agr. Sci.* 15: 272–283.

(10) PURI, A. N., CROWTHER, E. M., AND KEEN, B. A. 1925 The relation between the vapour pressure and water content of soils. *Jour. Agr. Sci.* 15: 68–88.

(11) RICHARDS, L. A. 1928 The usefulness of capillary potential to soil-moisture and plant investigators. *Jour. Agr. Res.* 37: 719–742.

(12) THOMAS, M. D. 1921 Aqueous vapor pressure of soils. *Soil Sci.* 11: 409–434.

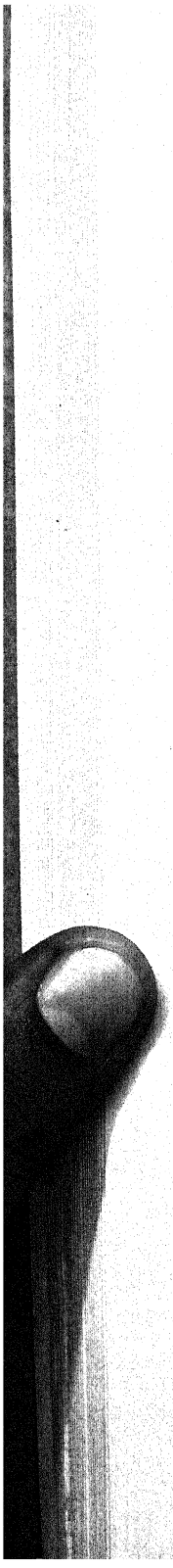
(13) THOMAS, M. D. 1924 Aqueous vapor pressure of soils: II. Studies in dry soils. *Soil Sci.* 17: 1–18.

(14) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1927 Soil-moisture conditions in relation to plant growth. *Plant Physiol.* 2: 71–82.

(15) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1928 Soil moisture at permanent wilting of plants. *Plant. Physiol.* 3: 355–357.

(16) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1931 The moisture equivalent as a measure of the field capacity of soils. *Soil Sci.* 32: 181–193.

(17) WASHBURN, E. W., AND HEUSE, E. O. 1915 Measurement of vapor-pressure lowering by air saturation method. *Jour. Amer. Chem. Soc.* 37: 309–321.



BASE EXCHANGE STUDIES ON THE PENNSYLVANIA JORDAN FIELD PLOTS[1]

F. G. MERKLE[2]

Pennsylvania Agricultural Experiment Station

Received for publication August 3, 1933

The field experiments of many experiment stations, notably Rothamsted, Woburn, Rhode Island, Pennsylvania, Ohio, Massachusetts, and New Jersey, are replete with examples of secondary or after effects of the long continued use of certain fertilizers upon the soil. These secondary effects of a fertilizer may be beneficial or detrimental and may manifest themselves in many different ways. The specific feature to be considered here is the possible effect upon the relative amounts of the various exchangeable cations held by the soil colloidal matter.

Numerous workers (3, 4, 7, 17, 18, 19, 21, 23, 30, 31, 33, 35, 36, 40, 41, 42, 43, 44, 45, 46, 47, 48, 52, 53, 54) have reported direct or indirect evidence that the long continued use of a given fertilizer on the same plot of soil brings about an alteration in the relative amounts of the various so-called replaceable ions. For the sake of brevity their findings will not be discussed here.

EXPERIMENTAL

The purpose, plan, and results of this field experiment are set forth in a series of reports and bulletins (39), therefore only a brief outline will be given here. Four tiers, of 36 plots each accommodate the rotation, which consists of corn, oats, wheat, timothy and clover. Corresponding plots in each tier are fertilized alike. The fertilizers are applied to the corn and wheat, as given in the summary table appended. In the original plan only three plots in each tier received lime—either alone or with manure. Manure and 2 tons burnt lime are applied to corn only on plot 22, and 2 tons burnt lime alone, on plot 23. Plot 34 receives 2 tons of ground limestone on the corn and wheat.

In 1921, 40 years after the experiment was started, it was decided to lime tiers 2 and 4 according to the individual requirement of each plot. Tier 1 and 3 remained unlimed with the exception of those plots previously mentioned.

Nearly all plots of tier 1, which perhaps is the most uniform in soil characters, were sampled in 1927, others in 1931, and still others in 1932. It became

[1] Publication authorized by the Director of the Pennsylvania Agricultural Experiment Station July 21, 1933, as Technical Paper No. 599.

[2] This investigation was carried out under the direction of Dr. J. A. Bizzell. The author takes this opportunity to express his appreciation and gratitude for the help extended during the prosecution of this work and for reviewing the manuscript.

apparent that plots 1 to 7 in tier 1 lacked uniformity; therefore, in 1932 plots 1, 2, 3, 4, and 8 in tier 3, also unlimed, were sampled and were found to be very homogenous. It was assumed that the liming of tiers 2 and 4 would mask the chief effects of fertilizers as it did at Rothamstead and at Ohio. Therefore, only four plots in tier 2, the ones most acid before liming, were sampled. Since yields had indicated that liming had completely restored the fertility on these acid plots, it was decided to see whether there was any fundamental difference in the exchange base content other than calcium.

The composite sample from each plot consisted of 12 borings equally distributed over the area. These were air dried, passed through a 1 mm. sieve, and stored in covered containers. For the determination of exchange base content 50 or 100 gm. of this air-dry soil were treated with 1 liter of neutral ammonium acetate. The advantages of this reagent for base exchange work have been clearly brought out by Schollenberger (46, 48).

Instead of the percolation method as outlined by Schollenberger the soil was shaken with successive small portions of ammonium acetate, allowed to settle, and the supernatant clear liquid poured on a filter. Finally the entire sample was transferred to the filter and leached with more reagent. Tests for calcium and pH showed that removal of these ions was complete.

Exchangeable hydrogen was, at first, determined by titrating the ammonium acetate filtrate potentiometrically with 0.1 *N* NH_4OH to pH 7.00. This method was used on about two-thirds of the samples. The results obtained by this method seemed high in many cases. Several soils which were definitely alkaline contained considerable exchange H by this method.

As the work progressed the advantage of direct titration seemed apparent (7, 10, 14, 15 22, 44, 49) It was tried and the following procedure adopted. Five 5-gm. samples of soil were placed in small vials (25 x 80 mm.). To a total volume of 10 ml. of liquid, 0, 2, 4, 6, or 8 m.e. of Ba $(OH)_2$ per 100 gm. of soil were added. The contents were very thoroughly stirred with a rod; then the vials were stoppered and allowed 72 hours to come to equilibrium. The hydrogen-ion concentration of the contents of each vial was determined potentiometrically. The H-ion concentrations were plotted against base added, and, from the curve obtained, the base required to bring the soil to pH 7 was determined. This was taken as the exchangeable hydrogen. The question arose whether one should use pH 7 or some higher value, pH 8 or 8.5, as the equilibrium value.

If the potentiometric and conductometric titrations of the Putnam clay sol of Baver (8) are examined it is apparent the reaction between the H-sol and the base is not instantaneous. To neutralize his H-sol immediately, 57 m.e. of base were required whereas after 3 months 60 or 62 m.e. apparently were required. When hydroxides of lithium, sodium potassium, calcium, and magnesium were added to equal quantities of sol at the rate of 57 m.e. per 100 gm. colloid, he obtained values below pH 7.00 in all cases, the lithium and sodium producing pH values close to 7.00, whereas potassium, calcium, and magnesium

gave the values 6.50, 5.95, and 6.19 respectively. If he had used 60 or 62 m.e. as the total exchange capacity per 100 gm. of colloid and allowed a longer time for the establishment of equilibrium, he would doubtless have obtained values above 7.00 for the lithium and sodium clays but very little above 7.00 for calcium and magnesium clay. Aarnio (1) produced single base clays by leaching with chlorides and found them to have the following pH values when all excess chloride was removed: Li 7.43, Na 7.20, K 7.02, Rb 6.60, Ca 7.77,

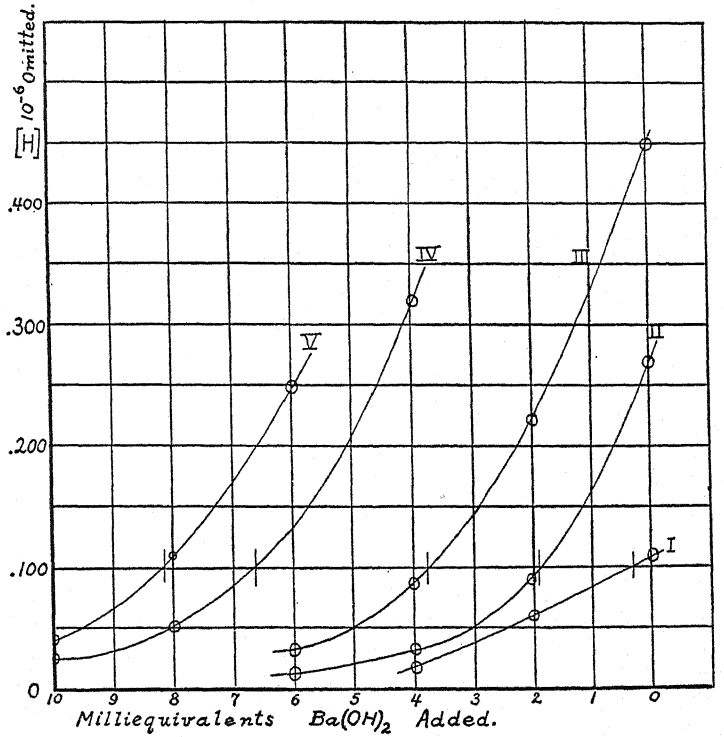


FIG. 1. TYPICAL TITRATION CURVES

I. Plot 5, 0.30 m.e. exchange H
II. Plot 14, 1.90 m.e. exchange H
III. Plot 15, 3.75 m.e. exchange H
IV. Plot 30, 6.60 m.e. exchange H
V. Plot 31, 8.10 m.e. exchange H

Mg 7.22, Ba 7.15. When a pure H-sol is titrated with base there is generally a break in the curve at neutralization, but when a natural soil containing bases as well as hydrogen is titrated no break is discernible. It is necessary, therefore, to choose some definite pH value as the neutralization point. Considering that the chief bases in the titrated residue are calcium, magnesium, and barium and that all of these have comparatively low solution pressures, it seemed best to choose the value 7.00, which is the one used by Bradfield (10)

when $Ba(OH)_2$ is used. Possibly a value of 7.5 might have been justified. A few typical titration curves are shown in figure 1. Similar curves were made for all samples.

When this direct titration method was used it was found that all soils having pH values above 7.00 contained no exchange hydrogen, whereas, as previously mentioned, ammonium acetate gave exchange H in soils which were definitely alkaline. Some idea of the comparative value of the two methods may be gained by plotting the pH value of the soils with the degree of saturation. The degree of saturation (100—H/T) was calculated for each method. This comparison is shown in figures 2 and 3. It is clear that for the soil samples in question a pH value of 7.00 represents 100 per cent saturation when the exchange hydrogen is measured by direct potentiometric titration and 75 to 80 per cent saturation when the exchange H is determined by titrating the ammonium acetate filtrate potentiometrically. Accordingly the direct titration method was adopted, and all calculations in the tables are based on it.

The hydrogen-ion concentration was determined with the quinhydrone electrode on the 1:2 soil—water suspension after the soil and water had been allowed 72 hours to come to equilibrium.

DETERMINATION OF BASES IN THE EXTRACT

The ammonium acetate extract was evaporated on the steam bath with a few drops of nitric acid. The residue was digested once or twice with 5 ml. of aqua regia, for several hours in a covered beaker, the amount and time depending on the quantity of organic matter. Following this it was dehydrated twice with hydrochloric acid, and the chlorides were filtered from the silica. Alumina and iron were removed as hydroxides but were not determined.

Calcium was precipitated in the warm solution containing ammonium chloride with an excess of saturated ammonium oxalate and estimated by titration with potassium permanganate.

The filtrate from the calcium determination was evaporated to dryness in a pyrex beaker, dried in the oven, and gently ignited in the beaker until all ammonium salts were volatilized. The residue was taken up with hydrochloric acid (1 + 4), digested a short time with 20–30 ml. of water, and filtered. The filtrate was made up to a definite volume. One-fourth was taken for the determination of potassium, one-fourth for sodium, and one-half for magnesium.

Magnesium was precipited as the phosphate and ignited.

Potassium was precipitated as the cobalt nitrite and determined volumetrically by titration with permanganate (34).

Sodium was precipitated as uranyl-zinc-sodium-acetate, dried, and weighed (6, 11).

Exchange ammonium was removed by leaching with 0.1 *N* HCl. The acid extract was made slightly alkaline with sodium hydroxide and ammonia distilled into standard acid.

When the work was started it was thought that only the limed plots con-

tained any carbonates. When this was investigated it was found that all plots, even the most acid ones, contained carbonate and that ammonium acetate removed a part of the calcium and magnesium in that form. Therefore, carbonates were determined on all samples, before and after leaching with ammonium acetate, and the difference was subtracted from the total calcium in the acetate extract. The latter figure was taken as the true exchangeable calcium, although it is doubtless true that a small part of the carbonate removed was present as magnesium carbonate.

DISCUSSION OF RESULTS

The analytical data are given in a single table in the appendix, together with the treatments and year of sampling. In order to bring out the outstanding

TABLE 1

Soil variation as shown by differences in check plots—Tier 1

(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 1	PLOT 8	PLOT 14	PLOT 24	PLOT 36	AVERAGE
Year sampled	1931	1931	1931	1931	1927	
Total Ca extracted	3.98	5.00	4.60	3.27	4.84	4.34
Exchange Ca	3.98	4.50	3.85	1.82	3.84	4.00
Mg	0.99	1.49	0.57	0.49	0.86	0.88
K	0.31	0.25	0.32	0.29	0.29	0.29
Na	0.12	0.11	0.09	0.05	0.12	0.10
NH_4	0.04	0.04	0.03	0.07	0.12	0.06
H	1.65	1.00	1.90	4.00	2.60	2.23
Total exchange capacity	7.09	7.39	6.76	6.72	7.83	7.15
Saturation, per cent	76.7	86.5	71.9	40.5	66.8	68.5
pH	6.6	6.8	6.6	6.0	6.2	
Carbonates	1.25	2.20	2.05	2.00	1.85	

effects, plots will be grouped side by side, those lying close to one another and in every way comparable being chosen for comparisons.

Soil variation as shown by differences in check plots. Plots 1, 8, 14, 24, and 36 receive no fertilizer, manure, or lime. They may be compared to bring out the soil variation from one end of the field to the other (table 1). The soil is not homogenous because of variations in thickness and density of the strata of limestone, which are tilted. An exposure occurs on plot 8 and accounts for the large quantity of calcium and magnesium on this plot. Plots 3, 5, 6 and especially plot 4, also have areas which are very close to the decomposing limestone. In general the results of these plots in tier 1 will not be used in comparisons but are reported as a matter of record. The acidity increases in plots 14 and 24 but decreases again in plot 36, which adjoins a farm road formerly surfaced with crushed limestone, the dust of which has blown on the plot.

The magnesium content parallels the calcium content and is a fair indication of the nearness to bed rock. The rock contains varying amounts of magnesium carbonate.

The potassium, sodium, and ammonium contents of the five check plots show no consistent variation from one end of the tier to the other.

The exchangeable hydrogen, pH, and degree of saturation are governed by the calcium and magnesium.

These check plots are well supplied with calcium and have an average pH value of about 6.50. Their yields have been poor due to lack of available phosphorus and possibly potassium rather than of available calcium and magnesium.

TABLE 2

Soil variation as shown by differences in grass strips bordering check plots—Tier 1

(Exchangeable bases in m.e. per 100 gm. soil)

Plot bordered.... Year sampled....	1 1931	8 1931	14 1931	24 1931	AVERAGE
Total Ca extracted	5.93	4.99	5.34	5.26	5.37
Exchange Ca	5.43	4.79	4.14	4.96	4.83
Mg	1.23	1.40	0.81	0.54	0.99
K	0.35	0.44	0.30	0.33	0.35
Na	0.11	0.13	0.09	0.10	0.11
NH_4	0.08	0.14	0.13	0.17	0.13
H	0.55	2.38	2.45	4.20	2.40
Total exchange capacity	7.75	9.28	7.92	10.30	8.81
Saturation, per cent	92.9	74.4	69.1	59.3	73.8
pH	6.8	6.4	6.5	6.5	
Carbonates	2.6	2.3	2.3	2.3	2.37

Certain grass strips adjacent to plots 1, 8, 14, and 24 were sampled by taking six borings on each side of the plot. The analyses of these samples are given in table 2. The grass strips show less variation than the adjacent cultivated plots, probably because erosion has been more severe on the plot than on the grass strip. The limestone outcrop which causes the Ca and Mg to be high in plot 8 does not appear in the grass strips adjacent to plot 8. The exchange magnesium varies from 0.54 to 1.40 m.e. and is again a good indication of nearness to bed rock.

Effect of cropping, or comparison between untreated plots with adjacent grass strips. This comparison should show the effect of cropping without fertilizer when a rotation of corn, oats, wheat, and clover is used. It brings out the effect of crop residues and of the increase in erosion and leaching, which occurs when land is left bare for certain months in the year. The comparison is not entirely fair since the bluegrass residues are not completely removed from the grass strips, thus allowing the nutrient bases to accumulate.

If we compare each plot with the adjacent grass strip we find (table 3), with one or two minor exceptions, that cropping has resulted in decreased calcium and magnesium contents, very little change in potassium and sodium, but a marked decrease in exchange ammonium. The latter ion stands out, being much higher on the grass strips than in any of the cultivated plots. The total exchange capacity is lowered by cultivation which has encouraged losses of organic matter by decomposition and erosion. In these comparisons we encounter an exception to the general rule, namely, a significant decrease in calcium and magnesium without an increase in hydrogen, which is probably due to a higher organic content on the grass strips.

TABLE 3

Comparison between untreated plots and grass strips between these plots—Tier 1

(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 1		PLOT 8		PLOT 14		PLOT 24	
	Strips	Plot	Strips	Plot	Strips	Plot	Strips	Plot
Total Ca extract	5.93	3.98	4.99	5.00	5.34	4.48	5.26	3.27
Exchange Ca	5.43	3.98	4.79	4.50	4.14	3.85	4.96	1.82
Mg	1.23	0.99	1.40	1.49	0.81	0.57	0.54	0.49
K	0.35	0.31	0.44	0.25	0.30	0.32	0.33	0.29
Na	0.11	0.12	0.13	0.11	0.09	0.09	0.10	0.05
NH_4	0.08	0.04	0.14	0.04	0.13	0.03	0.17	0.07
H	0.55	1.65	2.38	1.00	2.45	1.90	4.20	4.00
Total exchange capacity	7.75	7.09	9.28	7.39	7.92	6.76	10.30	6.72
Saturation, per cent	92.9	76.7	74.4	86.5	69.1	71.9	59.3	40.5
pH	6.8	6.6	6.4	6.8	6.5	6.6	6.5	6.0
Carbonates	2.6	1.25	2.3	2.2	2.3	2.05	2.3	2.0

Effects of manure. Barnyard manure at the rate of 6, 8, and 10 tons per acre is applied to the corn and oats on plots 16, 18, and 20. The base exchange data from these plots may be compared with those from check plots 14 and 24 (table 4). There seems to be a progressive change in the character of the soil from plot 14 to 24, the latter being definitely more acid. There is a slight indication that the use of manure has decreased the total calcium extracted in ammonium acetate but increased the exchange calcium. The net effect on calcium content of this soil is negligible. The exchange potassium is not increased in spite of the fact that considerable is added in the manure. The total exchange capacity and exchange hydrogen are definitely increased by the use of barnyard manure.

Manuring has tended to build up the magnesium reserve but not at all in proportion to the amounts used.

In conclusion it may be said that the use of manure has chiefly affected the exchange complex by increasing significantly the exchange H, Mg, and total exchange capacity.

Effect of continued use of lime compounds. Only three plots in tiers 1 and 3 have been limed. Plot 22 receives 6 tons of manure and 2 tons of burnt lime on the corn only; plot 23 is limed with 2 tons of burnt lime on corn only; and plot 34 receives 2 tons of ground limestone applied at the time of planting corn and wheat.

Plots 23 and 34 have yielded poorly for several years because of the lack of available phosphorus and possibly nitrogen. The plots have been limed greatly in excess of their needs, but it has never seemed desirable to change the treatments.

When soils are heavily limed repeatedly, as these plots are, they eventually come into equilibrium with calcium carbonate. We have a condition similar to a flask containing solid calcium carbonate in the bottom with a solution of

TABLE 4

Effects of manure—Tier 1

(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 14	PLOT 16	PLOT 18	PLOT 20	PLOT 24
Treatment	None	M6	M8	M10	None
Year sampled	1931	1927	1931	1931	1931
Total Ca extracted	4.60	4.21	2.59	3.22	3.27
Exchange Ca	3.85	4.21	2.19	2.62	1.82
Mg	0.57	0.89	0.96	0.66	0.49
K	0.32	0.27	0.33	0.38	0.29
Na	0.09	0.07	0.11	0.08	0.05
NH_4	0.03	0.15	0.08	0.08	0.07
H	1.90	6.00	5.50	4.70	4.00
Total exchange capacity	6.76	11.59	9.17	8.52	6.72
Saturation, per cent	71.9	48.2	40.0	44.9	40.0
pH	6.6	5.8	5.9	6.0	6.0
Carbonates	2.05	1.25	2.5	2.5	2.0

calcium bicarbonate charged with carbonic acid and, above this, air containing a large quantity of carbon dioxide. When this comes into equilibrium it will have a pH value somewhere between 8.2 and 8.4 depending on the temperature and partial pressure of CO_2 in the gas phase. The soil on both the burnt lime and limestone plots has been repeatedly sampled by Professors Holben and Jeffries and by the writer and has been found to fluctuate very little from the pH value 8.25 ± 0.05. However, the writer wished to determine whether or not values higher than these might be encountered immediately after ground burnt lime, CaO, was applied to a soil already containing an excess of calcium carbonate and therefore having a value close to 8.25.

The pH value of saturated lime water at 20°C. was found to be 12.38; therefore, if carbonation is not instantaneous we might expect values considerably above 8.25 for some time after liming. Plots 22, 23, and 34 were limed in the

spring of 1932. The soil was well supplied with moisture at the time, and rains were frequent but not excessive. The pH values were determined on the plots on a few occasions after liming (table 5). It is apparent that under these conditions carbonation is not immediate (28), because the pH value on the burnt lime plot is higher than the equilibrium value of calcium carbonate-

TABLE 5

Effect of liming with burnt lime and with limestone on the pH value of an alkaline soil—Tier 1*

		PLOT 22 CaO MANURE	PLOT 23 CaO	PLOT 34 $CaCO_3$
		pH	*pH*	*pH*
May 11	Moist	N.D.	9.9	8.66
June 15	Moist	8.48	8.72	8.48
June 15	Dried	8.32	8.32	8.19

* Lime applied May 6 and 7.

TABLE 6

Effect of lime compounds on the exchangeable bases—Tier 1

(m.e. per 100 gm. soil)

	PLOT 23*	PLOT 23	PLOT 24	PLOT 34*	PLOT 34	PLOT 36
Treatment	CaO	CaO	None	$CaCO_3$	$CaCO_3$	None
Year sampled	1932	1927	1931	1932	1931	1927
Total Ca extracted	56.2	17.80	3.27	68.0	17.10	4.84
Exchange Ca	11.10	8.0	1.82	15.85	11.60	3.84
Mg	0.91	0.46	0.49	0.95	0.49	0.86
K	0.14	0.38	0.29	0.30	0.38	0.29
Na	0.16	0.10	0.05	0.17	0.07	0.12
NH_4	0.07	0.07	0.09	0.07	0.05	0.12
H	0.00	0.00	4.00	0.00	0.00	2.60
Total exchange capacity	12.38	9.03	6.72	17.32	12.59	7.83
Saturation, per cent	Excess	Excess	40.5	Excess	Excess	66.8
pH	8.3	8.3	6.0	8.2	8.4	6.2
Carbonates	47.3	29.45	2.0	69.5	43.6	1.85

* Lime as CaO and $CaCO_3$ was applied in plots 23 and 34 respectively on May 6 and 7, 1932 before sampling.

carbonic acid-carbon dioxide. Injury from over-liming of a soil already neutral or alkaline seems quite possible, provided burnt lime or hydrate is used. Over-liming with carbonate seems less probable.

In table 6 the burnt lime plot 23 is compared with the adjacent check plot 24 and the carbonate of lime plot 34 is compared with the nearest check plot 36. So far as exchange bases are concerned the chief effects of continuous heavy liming have been to build up a large reserve of calcium in the exchange and

carbonate condition and, of course, to eliminate exchange hydrogen. The total exchange capacity as determined by addition is higher on these two plots than on any others in the tier. This might be expected since colloids increase their cation adsorption in the presence of hydroxyl ions (9, 13). However, Schollenberger and Dreibelbis (47) obtained the reverse effect by comparing the total exchange values of the limed and unlimed halves of the Ohio plots. So also did the writer obtain the opposite effect when the limed plots 21, 30, 31, and 32 of tier 2 are compared with the corresponding unlimed plots in tier 1 (table 14). In each of these latter cases there is a decrease of from 1 to nearly 3 m.e. in total capacity resulting from liming tier 2 in 1921. In the latter cases, where liming has caused a decrease in total capacity, the pH value is not above 7.00. In the former case, where excessive liming was practiced, the pH

TABLE 7

Effect of the superphosphate-muriate of potash treatment upon the exchangeable bases

(m.e. per 100 gm. soil)

	PLOT 8	PLOT 7	PLOT 14	PLOT 15	PLOT 24	PLOT 25	PLOT 36	PLOT 29
Treatment	0	P + K	0	P + K	0	P + K	0	P + K
Year sampled	1931	1931	1931	1931	1931	1931	1927	1932
Total Ca extract	5.00	4.48	4.60	3.82	3.27	3.00	4.84	2.96
Exchange Ca	4.50	4.13	3.85	3.12	1.82	3.00	3.84	2.96
Mg	1.49	1.55	0.57	0.49	0.49	0.48	0.86	0.88
K	0.25	0.49	0.32	0.46	0.29	0.50	0.29	0.53
Na	0.11	0.21	0.09	0.11	0.05	0.05	0.12	0.48
NH_4	0.04	0.05	0.03	0.07	0.07	0.21	0.12	0.16
H	1.00	2.30	1.90	3.75	4.00	6.40	2.60	4.45
Total exchange capacity	7.39	8.73	6.76	8.00	6.72	10.64	7.83	9.46
Saturation, per cent	86.5	73.6	71.9	53.2	40.5	39.9	66.8	53.0
pH	6.8	6.7	6.6	6.35	6.0	5.2	6.2	6.1
Carbonates	2.2	2.8	2.05	2.2	2.0	1.35	1.85	1.16

values were about 8.3. Exchange magnesium has been increased by liming, but no significant difference appears with respect to the other cations.

Influence of superphosphate-muriate of potash treatment on exchangeable base content. Plots 7, 15, 25, and 29 receive 300 pounds of 16 per cent superphosphate and 200 pounds of muriate of potash twice in the rotation. The quantity of potash is believed to be excessive. Nevertheless, this combination has given the largest net financial returns of any combination used, with the exception of those receiving barnyard manure. Fortunately for study, each of these plots lies adjacent to, or close to, a check plot. The comparisons are given in table 7. In making such comparisons we must keep in mind that the yields on the nothing plots have been small for several years, while those on the PK plots have been large, hence there will be a greater removal of the nutrient bases on the PK plots. Furthermore superphosphate contains calcium as phosphate and sulfate, and this should tend to maintain the supply of this element.

The total exchange capacity has been increased by the PK treatment in every instance, doubtless as a result of the higher organic content which these plots have attained. At the same time active organic matter has declined on the nothing plots on account of the smaller crop residues.

The total calcium extracted with ammonium acetate is significantly lower in every case as a result of the PK treatment. This is true in spite of the fact that calcium is added in the superphosphate. The exchange calcium is also decreased by this fertilizer combination in all except one case. Nothing definite can be said about the exchange magnesium, but potassium has been nearly doubled, as would be expected. Concomitant with the decrease of calcium we have a positive gain in hydrogen in the colloidal matter. The PK treated plots are less saturated with bases and have slightly lower pH values. It is

TABLE 8

Influence of superphosphate alone upon the exchangeable bases

(m.e. per 100 gm. soil)

	PLOT 1	PLOT 3	PLOT 8
Treatment	None	P	None
Year sampled	1932	1932	1932
Total Ca extracted	4.42	4.49	4.24
Exchange Ca	3.57	3.64	3.74
Mg	1.68	1.14	1.33
K	0.30	0.14	0.23
Na	0.11	0.11	0.12
NH_4	0.04	0.02	0.06
H	2.00	2.70	2.10
Total exchange capacity	7.70	7.75	7.58
Saturation, per cent	74.0	62.7	72.3
pH	6.5	6.2	6.5
Carbonates	1.4	1.45	1.15

not altogether fair to compare PK plot 29 with the check 36 because the latter receives limestone dust from the highway, but if we compare it with check plot 24, which is closer to it, the conclusions are nearly the same.

No explanation is given for the high exchange sodium content on PK plot 29, and no importance is claimed for it. The duplicate determinations on this plot gave 0.50 and 0.46 m.e. of sodium.

Effect of superphosphate alone. The PK combination was shown to cause a decrease in calcium and an increase in hydrogen, but it was not possible to determine which salt was responsible for the change. Plot 3 of tier I receives superphosphate alone, but the soil is not uniform enough to be considered. However, the first eight plots in tier 3, also unlimed, are very homogenous, hence plot 3 receiving superphosphate alone is compared with check plots 1 and 8 tier 3 (table 8). Analyses of the data indicate that superphosphate has had very little effect upon the reactive calcium but it has produced a

significant increase in exchange hydrogen. This is in agreement with the findings of Schollenberger and Dreibelbis (47) and of Page and Williams (36). Exchange magnesium and potassium are decreased by the use of superphosphate alone, doubtless because of the greater removal in crops, which have been sizeable on this plot. The phosphate has decreased the state of saturation with bases by about 10 per cent and increased the hydrogen-ion concentration. It is concluded that superphosphate does tend to increase acidity even though it increases the active calcium in the soil. The effect is a small one for 50 years of continuous use.

Comparison between raw bone and acidulated phosphates. From theoretical considerations it would seem that raw bone might decrease acidity if the PO_4,

TABLE 9

Comparison between ground bone and superphosphate upon the content of exchangeable bases

(m.e. per 100 gm. soil)

	PLOT 6*	PLOT 12	PLOT 17	PLOT 19	PLOT 35
Treatment	NK	NPK	NPK	NPK	NPK
P carrier	None	Bone	Superphosphate	Superphosphate	Bone
Year sampled	1931	1931	1931	1931	1932
Total Ca extracted	3.47	4.31	1.66	1.74	5.11
Exchange Ca	3.32	3.21	0.81	1.34	5.11
Mg	1.28	1.37	0.47	0.30	1.57
K	0.66	0.43	0.44	0.40	0.56
Na	0.18	0.14	0.12	0.08	0.21
NH_4	0.05	0.05	0.08	0.08	0.10
H	2.55	2.90	6.20	6.40	1.95
Total exchange capacity	8.04	8.10	8.12	8.60	9.50
Saturation, per cent	68.3	64.2	23.7	25.6	79.5
pH	6.6	6.6	5.6	5.5	5.6
Carbonates	1.60	6.40	2.90	2.10	1.67

* Not a good comparison plot. Probably influenced by nearness to limestone in places.

HPO_4, or H_2PO_4 ion is assimilated in greater equivalent quantity than calcium. On the other hand superphosphate contains an acid salt $Ca\ H_4(PO_4)_2$ with three equivalents of PO_4 for each equivalent of calcium. It should increase acidity and was shown to in plot 3 of tier 3.

To compare these two carriers of phosphorus we may use plots 12 and 35 vs. 17 and 19 in tier 1. Plots 12 and 35 each receive 30 pounds of nitrogen in blood, 48 pounds of P_2O_5 in ground bone, and 100 pounds of K_2O in muriate of potash. Plots 17 and 19 are treated like 12 and 35 except that they receive their phosphorus in superphosphate and have slightly different amounts of blood—17 receives 24 pounds, and 19 receives 48 pounds of nitrogen (table 9).

Ground bone appears to have left a residue of calcium in the soil, hence even though slightly more of the acid forming blood is applied to bone plots 12

and 35 than to the superphosphate plot, still there is definitely more calcium in the bone treated plots. The exchange hydrogen, saturation values, and pH values all prove that superphosphate increases soil acidity as compared with ground bone. The exchange magnesium is likewise lower in the superphosphate plots.

Further evidence is gained when plot 6, which receives blood and muriate, is compared with plot 17, which is fertilized with superphosphate in addition, or with plot 12 or 35, both of which receive bone in addition. These comparisons prove that bone builds up a reserve of calcium with little or no effect upon the exchange hydrogen and pH value. It is also apparent that superphosphate does increase soil acidity. The nitrogen-potash plot 6 appears to contain a

TABLE 10

Effect of dried blood upon the exchangeable bases

(m.e. per 100 gm. soil)

Tier and plot Treatment N per acre, lbs	3/1 O 0	3/2 N 24	3/8 O 0	1/15 PK 0	1/17 NPK 24	1/19 NPK 48	1/21 NPK 72	1/25 PK 0
Total Ca extracted	4.42	3.40	4.24	3.82	1.66	1.74	1.72	3.00
Exchange Ca	3.57	2.68	3.74	3.12	0.81	1.34	0.92	3.00
Mg	1.68	1.14	1.33	0.49	0.47	0.30	0.29	0.48
K	0.30	0.25	0.23	0.46	0.44	0.40	0.48	0.50
Na	0.11	0.11	0.12	0.11	0.12	0.08	0.14	0.05
NH_4	0.04	0.04	0.06	0.07	0.08	0.08	0.11	0.21
H	2.00	3.44	2.10	3.75	6.20	6.40	7.40	6.40
Total exchange capacity	7.70	7.66	7.58	8.00	8.12	8.60	9.34	10.64
Saturation, per cent	74.0	55.1	72.3	53.2	23.7	25.6	20.8	39.9
pH	6.5	5.8	6.5	6.35	5.6	5.5	5.5	5.2
Carbonates	1.40	1.50	1.15	2.20	2.90	1.34	2.1	1.35

reserve of magnesium and potassium which is due to the low removals in crops from this plot.

Schollenberger's data (47) reveal no appreciable difference between bone and superphosphate in the quantity of adsorbed ions.

Effect of dried blood used alone. Dried blood contains 16 per cent nitrogen, most of which is easily nitrified. Its total ash content is low, consequently, on decay, carbonic and nitric acids are formed, and acids even when present in low concentration possess high base exchange powers due to the high energy of absorption of the hydrogen ion. We therefore expect a considerable loss of bases as a result of the use of dried blood without lime. This is shown to be the case in the comparisons which follow:

Table 10 is a comparison between the untreated check plots 1 and 8 and the blood treated plot 3, in tier 3. The yields on plot 3 (blood) have been poor, in fact lower than the average of the five check plots. Consequently, any decrease in bases as compared with the checks is due to leaching rather than to

crop removal. Dried blood has caused a decided decrease in the quantity of calcium and magnesium and a corresponding increase in replaceable hydrogen. The remaining exchangeable cations are unaffected.

In tier 1 it is possible to compare three rates of dried blood with the nearest PK plots; the only variant being the presence and amount of blood. Plots 17, 19, and 21 receive 24, 48, 72 pounds of nitrogen respectively in blood, twice in the rotation. The use of blood, as might be expected, has caused a decided decrease in total extracted calcium and exchangeable calcium to about one-half or one-third of that in the nearest PK plots. However, there is no evidence that the larger amounts of blood have been more effective in reducing the active calcium than have smaller amounts, or to put it another way, the smaller amounts of blood have reduced the calcium to such a low figure that larger amounts show no added effect. It is logical to assume that during the 50 years more nitrogen has found its way into the drainage water as HNO_3 in plot 21 than in plot 17. It is obviously impossible to calculate in advance how much lime must accompany a given quantity of blood to keep a soil in its original state of saturation.

The exchange magnesium is also decreased by the use of blood. No significant differences are to be found in the quantity of adsorbed potassium. Equal, large amounts of this element have been added to all plots in this comparison; and in spite of the large amount removed in crops there are now 0.40 to 0.50 m.e. present.

The PK plots 15 and 25 are now 40 to 50 per cent saturated with bases, whereas those receiving blood in addition are only 20 to 25 per cent saturated.

Organic nitrogen has produced upon the exchange picture of this soil a profound effect that is now showing itself in reduced yields on these plots even though heavily fertilized. Liming on tiers 2 and 4 has completely restored this soil in character of complex and in yields.

Effect of the use of nitrate of soda. According to theoretical reasoning and the observations handed down to us from the majority of field experiments (19) nitrate of soda either should have no effect or should reduce acidity slightly. Both ions of this salt leach readily. The sodium will seek the liquid phase and leach out with any strong acid radicals, which may be added to, or formed in, the soil.

Plots 26, 27, and 28, which receive nitrate of soda equivalent to 24, 48, and 72 pounds of nitrogen, and the adjacent PK plots 25 and 29 are used in this comparison. The only variable is the presence and amount of nitrate of soda. This comparison is given in table 1. The use of nitrate of soda has had no appreciable effect upon the quantity of any ion except hydrogen, which has been slightly reduced. Sodium has not been retained; therefore, the total exchange capacity of the soda-treated soils is lowered by 2 or 3 m.e. It is logical to assume that sodium has peptized some of the colloidal matter and caused it to be translocated to lower horizons or removed in the drainage water.

These effects of nitrate of soda agree exactly with those reported by Schollenberger (47).

No explanation is offered for the high sodium content found in the PK plot 29. Pierre (41, 42) has reported a tendency for nitrate of soda to increase alkalinity as shown by pH values and by degree of saturation, but his work was conducted in greenhouse pots, in which no leaching took place. Under such conditions a sodium residue is permitted to accumulate.

Influence of sulfate of ammonia. This fertilizer salt is well known for its effects upon soil reaction, although it should be pointed out that for the first 8 years of this experiment (39) the sulfate plots outyielded the nitrate or blood plots and it was not until 20 years had elapsed that the yield dropped

TABLE 11

Effects of nitrate of soda upon the exchangeable bases

(m.e. per 100 gm. soil)

	PLOT 25	PLOT 26	PLOT 27	PLOT 28	PLOT 29
Treatment	PK	NPK	NPK	NPK	PK
N per acre, lbs	0	24	48	72	0
Year sampled	1927	1931	1931	1931	1932
Total Ca extracted	3.00	3.18	3.43	2.91	2.96
Exchange Ca	3.00	2.98	3.33	2.76	2.96
Mg	0.48	0.54	0.52	0.35	0.88
K	0.50	0.41	0.42	0.48	0.53
Na	0.05	0.14	0.10	0.11	0.48
NH_4	0.21	0.10	0.09	0.08	0.16
H	6.40	4.20	4.00	4.20	4.45
Total exchange capacity	10.64	8.37	8.46	7.98	9.46
Saturation, per cent	39.9	49.8	52.7	47.4	53.0
pH	5.2	6.0	6.1	6.0	6.0
Carbonates	2.45	1.60	1.2	1.05	1.3

materially on account of acidity. Furthermore, one treatment with lime on tiers 2 and 4 has completely restored the fertility on these very acid plots.

The theoretical reasoning has been put forth by Pierre (41, 42), by Allison (2), and by Kappan, (24, 25) that if all the ammonia in sulfate of ammonia is transformed into nitric acid, each equivalent of sulfate of ammonia produces two equivalents of acid and on this basis the lime needs may be calculated. Under field conditions when sulfate of ammonia is applied to different crops and with varying climatic conditions, we are confronted with such questions as: What proportion of the total nitrogen is assimilated in the ammonia form and what part in the nitrate form (50), and is this the same for all plants? What proportion of the nitrogen which leaches out is in the form of nitrate salts and what part is in the form of nitric acid? Can plants assimilate nitric acid (2), that is, can they adsorb anions in excess of cations? All these ques-

tions made it utterly impossible to calculate the amount of lime needed under field conditions for each 100 pounds of sulfate of ammonia.

Plots 29, 30, 31, and 32 in tier 1 were chosen for this comparison. Plot 29 is the PK plot, the remaining plots receive, in addition to PK, varying amounts of sulfate of ammonia. Plot 29 was sampled in 1932; plots 30, 31, and 32 were sampled in 1931; and plot 32 was also sampled in 1927. These comparisons are set forth in table 12.

Sulfate of ammonia has produced the most marked effects of any fertilizer used in this experiment. The total calcium extractable and the exchange calcium have been reduced to one-third by the use of 24 pounds of nitrogen in sulfate of ammonia twice in the rotation, and to about one-fourth and one-

TABLE 12

Effects of sulfate of ammonia upon the quantity of exchangeable bases

(m.e. per 100 gm. soil)

	PLOT 29	PLOT 30	PLOT 31	PLOT 32	PLOT 32
Treatment	PK	NPK	NPK	NPK	NPK
N per acre, lbs.	0	24	48	72	72
Year sampled	1932	1931	1931	1931	1927
Total Ca extracted	2.96	1.31	0.73	0.75	0.45
Exchange Ca	2.96	1.31	0.38	0.65	0.45
Mg	0.88	0.31	0.33	0.31	0.59
K	0.53	0.33	0.38	0.38	0.29
Na	0.48	0.15	0.11	0.07	0.18
NH_4	0.16	0.11	0.10	0.07	0.14
H	4.45	6.60	8.10	8.80	8.70
Total exchange capacity	9.46	8.81	9.40	10.28	10.33
Saturation, per cent	53.0	25.0	13.8	14.5	15.5
pH	6.1	5.3	4.96	4.70	4.55
Carbonates	1.3	0.9	1.3	0.7	0.75

sixth, respectively, by the 48-pound and 72-pound applications. From 75 to 85 per cent of all the exchange ions are hydrogen ions, but calcium is not the only base affected. Magnesium and even potassium have been significantly diminished, when compared with the nearest PK plot. This is true in spite of the fact that equal, large amounts of potash have been used and that the crop removals on the most acid plots have not been as great as on the PK plots. The average exchange potassium content of the three corresponding blood plots is 0.44, and of the three nitrate plots 0.44, whereas the three sulfate of ammonia plots average only 0.36. This difference is not large but is quite consistent. It appears impossible to calculate the lime needs from any factor or formula, since the 48-pound application has depleted the calcium as much as the 72-pound treatment. It seems logical that the more calcium that is present in the soil the more rapidly it will be removed, and that, when the active

calcium content is reduced to a very low figure, the nitric and sulfuric acid may leach through as acids or even as iron and alumina salts. This was well brought out in a previous paper by the writer (32), in which the base exchange content of samples drawn in 1915 was compared with that of those drawn in 1927. Some data are reproduced in table 13. During the 12-year period from 1915 to 1927 the loss of calcium and magnesium has been no greater on the sulfate of ammonia plot 32 than upon the phosphorus-potash plot 25. This is because early in the history of the experiment the sulfate of ammonia had replaced the readily replaceable calcium with hydrogen ions.

It is interesting to note that some carbonates are present even in the most acid plot, No. 32. This plot has had a pH value of 4.5 to 4.7 for several years.

TABLE 13

Comparison of different nitrogen carriers with the PK plot in 1915 and 1927

(Exchangeable bases in m.e. per 100 gm. soil)

	PK 25	NPK $NaNO_3$ 28	NPK Blood 21	NPK $(NH_4)_2SO_4$ 32
Calcium 1915	4.07	3.73	3.34	1.51
Calcium 1927	3.00	3.12	2.30	0.45
12-year change	−1.07	−0.61	−1.04	−1.06
Magnesium 1915	0.75	0.81	0.74	0.87
Magnesium 1927	0.48	0.55	0.55	0.59
12-year change	−0.27	−0.26	−0.19	−0.28
Hydrogen 1915*	5.25	4.22	5.87	6.02
Hydrogen 1927	6.05	5.50	7.22	8.65
12-year change	+0.80	+1.28	+1.35	+2.63

* Exchange hydrogen determined by ammonium acetate extraction.

The carbonate content of the sulfate of ammonia plots is lower than that of any other plot in this field experiment.

There is no evidence that sulfate of ammonia causes the NH_4 ion to accumulate in the colloidal complex.

It is quite probable that these plots will not attain pH values much lower than 4.5 even though the use of sulfate of ammonia be continued. Under the conditions obtaining here, the nitric and sulfuric acids added and formed from each application will leach through as acids or as iron and aluminum salts, and the pH value will revert to that of humic and silicic acids. For a few months after fertilization the pH value may possibly run lower than 4.5. This has not been investigated.

The base exchange picture on these sulfate-treated plots is decidedly different from that of those receiving P and K and consists in the substitution of H for not only Ca but for Mg and K also.

Effect of muriate of potash. It was previously shown that the PK treatment had acid-producing tendencies but it remained to be determined which salt in this combination was responsible. Then it was shown that superphosphate alone tended to increase the replaceable hydrogen but not to reduce the replaceable calcium materially. What is the effect of the potash salt?

Plot 4 in tier 1 might have been chosen to make this comparison but, since it is probably the least uniform of all plots sampled in this work, plot 4, KCl alone, in tier 3 was compared with check plots 1 and 8 in the same tier (table 14). The addition of K as KCl has caused a reduction in total calcium extracted and in exchangeable calcium, no effect upon magnesium, but a decided increase in potassium. In this case K rather than H seems to have replaced the Ca, for there is no increase in replaceable H. Yields have been low on this plot because

TABLE 14

Effects of muriate of potash on the content of exchangeable bases

(m.e. per 100 gm. soil)

Tier and plot Treatment Year sampled	3/1 O 1932	3/4 K 1932	3/8 O 1932	1/2 N 1927	1/6 NK 1931
Total Ca extracted	4.42	3.64	4.24	5.69	3.47
Exchange Ca	3.57	2.99	3.74	5.69	3.32
Mg	1.68	1.39	1.33	1.83	1.28
K	0.30	0.68	0.23	0.23	0.66
Na	0.11	0.14	0.12	0.20	0.18
NH_4	0.04	0.06	0.06	0.05	0.05
H	2.00	2.10	2.10	0.00	2.55
Total exchange capacity	7.70	7.36	7.58	8.00	8.04
Saturation, per cent	74.0	71.5	72.3	Excess	68.3
pH	6.5	6.5	6.5	7.2	6.6
Carbonates	1.40	1.45	1.15	1.85	1.6

of lack of available phosphorus, hence the large reserve of potassium. Any plot in this experiment which receives no phosphate, yields poorly. The decrease in Ca either has been insufficient to make any difference in pH value or it is counterbalanced by the more highly dissociating potassium.

In tier 1, plot 2 may be compared with plot 6. Both receive dried blood equal to 24 pounds of nitrogen, the variable being muriate of potash. Although these results cannot be regarded as very conclusive, because of the soil irregularity previously mentioned, they do tend to confirm the conclusion drawn from tier 3, plot 1, 4, 8, namely, that the addition of KCl causes calcium depletion and the building up of a reserve of exchange K.

The same conclusions are strengthened by comparing plot 5, blood and superphosphate, with plot 12, blood, bone, and muriate, though in this case the source of phosphorus is different in the two plots compared.

Effect of recent liming on certain very acid plots. In 1921, tier 2 was limed

according to the lime requirement as determined by Prof. J. W. White and his associates. The yields on the acid plots were quickly restored. There was some reserve of phosphorus, due to a long period of low yields, but no special reserve of magnesium and potassium. It is interesting to find the chief effect brought about by liming these very acid plots. A few of the most acid plots —the sulfate of ammonia plots and the plot receiving the highest blood treatment—have been compared with the corresponding unlimed plots in tier 1 (table 15).

In each of these acid plots, liming restored the exchangeable calcium from almost nothing in tier 1 to from 4 to 6 m.e. in tier 2. It would appear that for this soil from 4.0 to 4.5 m.e. of calcium in the exchange form are necessary to produce neutrality.

TABLE 15

Effect of recent liming on certain very acid plots—Tiers 1 and 2

	PLOT 21		PLOT 30		PLOT 31		PLOT 32	
Treatment	NPK		NPK		NPK		NPK	
N per acre, lbs.	Blood, 72 lbs. N		Sulfate, 24		Sulfate, 48		Sulfate, 72	
Tier and liming	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed	Unlimed	Limed
Year sampled	1931	1932	1931	1932	1931	1932	1931	1932
Total Ca extract	1.72	5.82	1.31	7.13	0.73	6.70	0.75	6.60
Exchange Ca	0.92	5.82	1.31	3.90	0.38	5.23	0.65	4.65
Mg	0.29	0.89	0.31	1.53	0.33	1.51	0.31	1.33
K	0.48	0.45	0.33	0.32	0.38	0.37	0.38	0.53
Na	0.14	0.13	0.15	0.14	0.11	0.12	0.07	0.12
NH_4	0.11	0.06	0.11	0.04	0.10	0.07	0.07	0.15
H	7.40	0.89	6.60	0.00	8.10	0.00	8.80	0.00
Total exchange capacity	9.34	8.24	8.81	5.93	9.40	7.30	10.28	6.78
Saturation, per cent	20.8	89.2	25.0	Excess	13.8	Excess	14.5	Excess
pH	5.5	6.8	5.3	7.3	4.96	7.15	4.70	7.00
Carbonates	2.10	1.1	0.90	7.03	0.95	2.87	0.70	2.80

The magnesium, which had likewise been reduced to around 0.29 to 0.33 m.e. by acid-producing fertilizers was restored by the liming materials used, which contain small amounts of magnesium.

Potassium, sodium, and ammonia seem not to have been materially influenced by liming.

In only one case, that of plot 30 in tier 2, is there any marked excess of calcium carbonate over the general average of all the plots. In this case we have limed in excess of the true lime requirement.

These treatments have restored the yields. It would have been highly instructive to see what effects fractional neutralization would have had on yields and on exchange complex.

In choosing these plots in tier 1 and 2, it was thought that we might shed some light on the important question of whether or not all the H must be

replaced in the complex for best results with these crops. It was shown that the H was replaced, at least according to the methods used, but whether or not smaller amounts of lime would give equal yields is not demonstrated.

Comparison of nitrogen carriers. The three nitrogen carriers, dried blood, nitrate of soda, and sulfate of ammonia, each in sufficient quantity to carry 72 pounds of nitrogen per acre twice in the rotation are compared with one another and with the nearest PK plots. In this comparison the PK treatments are alike throughout. To show the trend of the soil as well as our data permit, the plots are arranged in table 16 in the order in which they occur in the field.

The comparisons show that nitrate of soda has very little effect upon the exchange Ca, Mg, and H; upon saturation; or upon pH value. Dried blood

TABLE 16

A comparison of nitrogen carriers—Tier 1, 72 pounds N per acre

(Exchangeable bases in m.e. per 100 gm. soil)

	PLOT 15	PLOT 21	PLOT 25	PLOT 28	PLOT 29	PLOT 32
Treatment	PK	NPK	PK	NPK	PK	NPK
N carrier	0	Blood	0	Nitrate	0	Sulphate
Year sampled	1931	1931	1927	1931	1932	1931
Total Ca extract	3.82	1.72	3.00	2.91	2.96	0.75
Exchange Ca	3.12	0.92	3.00	2.76	2.96	0.65
Mg	0.49	0.29	0.48	0.35	0.88	0.31
K	0.46	0.48	0.50	0.48	0.53	0.38
Na	0.11	0.14	0.05	0.11	0.48	0.07
NH_4	0.07	0.11	0.21	0.08	0.16	0.07
H	3.75	7.40	6.40	4.20	4.45	8.80
Total exchange capacity	8.00	9.34	10.64	7.98	9.46	10.28
Saturation, per cent	53.2	20.8	39.9	47.4	53.0	14.5
pH	6.35	5.5	5.2	6.0	6.1	4.7
Carbonates	2.20	2.10	2.45	1.1	1.3	0.70

decidedly increases acidity, and sulfate of ammonia greatly affects not only Ca and Mg but exchange K as well.

Relation between pH value and degree of saturation. The pH value of a soil is a measure of the ratio between the active cations and anions in the soil solution, which in turn are controlled by the adsorbed ions. One might expect, therefore, for any given soil, a fairly definite relationship between the degree of saturation and the pH value. Conrey and Schollenberger (16) obtained a fair relationship between pH value and degree of saturation of the various horizons of the Claremount soil profile. If the data of Walker, Firkins, and Brown (51) are examined with this in view a very good correlation is found.

Since both values were determined in this work it was thought well to plot one against the other to see how close the relationship is for this soil. Figure 3 shows this relationship for degrees of saturation calculated from exchange

hydrogen as determined by titrating the ammonium acetate extract, and figure 2 shows the relationship when exchange hydrogen is determined by direct titration of the soil with $Ba(OH)_2$.

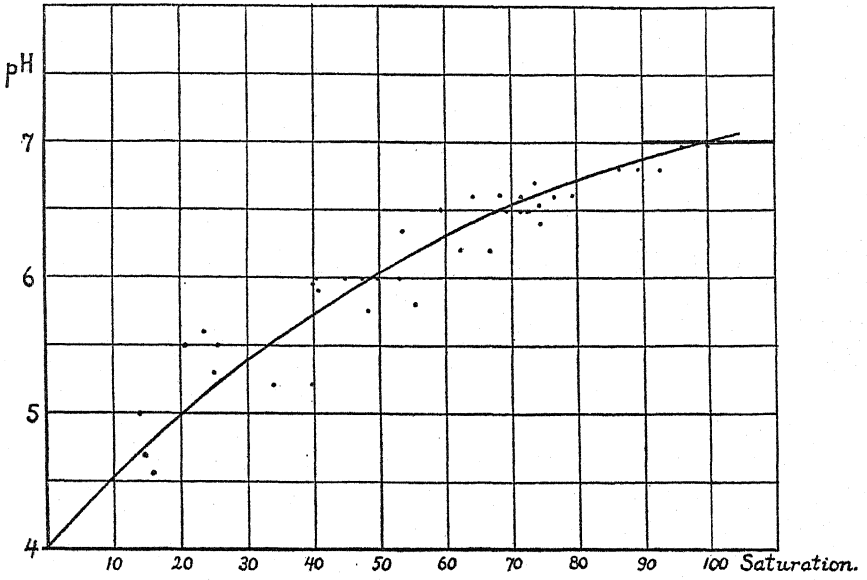


FIG. 2. RELATION BETWEEN pH AND SATURATION
Exchange H by direct titration

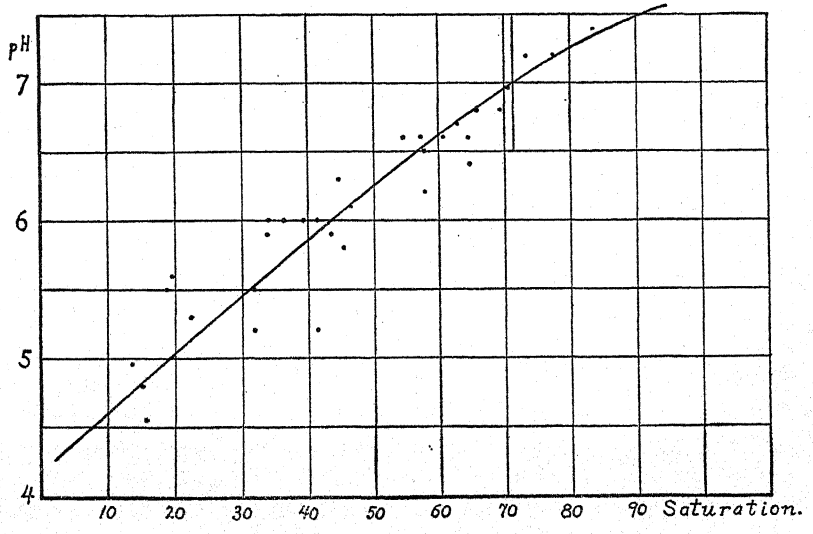


FIG. 3. RELATION BETWEEN pH AND DEGREE OF SATURATION
Exchange H by ammonium acetate

TABLE 17

Summary table showing the exchangeable cations in the Pennsylvania Jordan soil fertility plots after 45–50 years of continuous cropping and fertilizing

(Exchangeable ions in m.e. per 100 gm. soil)

TIER	PLOT	FERTILIZERS ALTERNATE YEARS	TOTAL Ca EXTRACTED	Ca	Mg	K	Na	NH_4	H TITRATION	H NH_4Ac	TOTAL	TOTAL CO_3	PER CENT SATURATION	pH	YEAR SAMPLED
1	1	None, strips	5.93	5.43	1.23	0.35	0.11	0.08	0.55	3.17	7.75	2.60	92.9	6.8	1931
1	1	None	3.98	3.98	0.99	0.31	0.12	0.04	1.65	3.50	7.09	1.25	76.7	6.6	1931
1	2	Nb24	5.69	5.69	1.83	0.23	0.20	0.05	0.00	2.30	8.00	1.85	100+	7.2	1927
1	3	P	6.31	6.21	2.02	0.29	0.10	0.09	0.00	3.15	8.71	1.45	100+	7.1	1927
1	4	K	6.31	6.31	3.13	0.31	0.29	0.06	0.00	2.00	10.10	6.15	100+	7.4	1927
1	5	Nb24, P	5.48	4.98	1.82	0.34	0.09	0.07	0.30	3.10	7.60	2.80	96.1	7.0	1931
1	6	Nb24, K	3.47	3.32	1.28	0.66	0.18	0.05	2.55	4.05	8.04	1.60	68.3	6.6	1931
1	7	P, K	4.48	4.13	1.55	0.49	0.21	0.05	2.30	3.80	8.73	2.80	73.6	6.7	1931
1	8	None, strips	4.99	4.79	1.40	0.44	0.13	0.14	2.38	3.70	9.28	2.30	74.4	6.4	1931
1	8	None	5.00	4.50	1.49	0.25	0.11	0.04	1.00	3.32	7.39	2.20	86.5	6.8	1931
1	12	Nb30, Pb, K	4.31	3.21	1.37	0.43	0.14	0.05	2.90	4.40	8.10	6.40	64.2	6.6	1931
1	14	None, strips	5.34	4.14	0.81	0.30	0.09	0.13	2.45	3.99	7.92	2.30	69.1	6.5	1931
1	14	None	4.60	3.85	0.57	0.32	0.09	0.03	1.90	4.22	6.76	2.05	71.9	6.6	1931
1	15	P, K	3.82	3.12	0.49	0.46	0.11	0.07	3.75	5.27	8.00	2.20	53.2	6.35	1931
1	16	M6	4.21	4.21	0.89	0.27	0.07	0.15	6.00	6.75	11.59	1.25	48.2	5.8	1927
1	17	Nb24, P, K	1.66	0.81	0.47	0.44	0.12	0.08	6.20	7.75	8.12	2.90	23.7	5.6	1931
1	18	M8	2.59	2.19	0.96	0.33	0.11	0.08	5.50	7.15	9.17	2.50	40.0	5.95	1931
1	19	Nb48, P, K	1.74	1.34	0.30	0.40	0.08	0.08	6.40	7.91	8.60	2.10	25.6	5.5	1931

1	20	M-10	3.22	2.62	0.66	0.38	0.08	0.08	4.70	6.63	8.52	2.50	44.9	6.0	1931
1	21	Nb72, P, K	1.72	0.92	0.29	0.48	0.14	0.11	7.40	8.40	9.34	2.10	20.8	5.5	1931
1	22	M6, CaO	52.10	12.80	1.37	0.26	0.22	0.05	0.00		14.70	42.3	100+	8.3	1932
1	23	CaO	17.80	8.00	0.46	0.38	0.10	0.09	0.00		9.03	29.45	100+	8.3	1927
1	23	CaO	56.20	11.10	0.91	0.14	0.16	0.07	0.00		12.38	47.30	100+	8.3	1932
1	24	None, strips	5.26	4.96	0.54	0.33	0.10	0.17	4.20	4.61	10.30	2.30	59.3	6.5	1931
1	24	None	3.27	1.82	0.49	0.29	0.05	0.07	4.00	5.17	6.72	2.00	40.5	6.0	1931
1	25	P, K	3.00	3.00	0.48	0.50	0.05	0.21	6.40	6.05	10.64	2.45	39.9	5.2	1927
1	26	Nn24, P, K	3.18	2.98	0.54	0.41	0.14	0.10	4.20	5.85	8.37	1.60	49.8	6.05	1931
1	27	Nn48, P, K	3.43	3.33	0.52	0.42	0.10	0.09	4.00	5.10	8.46	1.20	52.9	6.1	1931
1	28	Nn72, P, K	3.12	3.07	0.55	0.39	0.08	0.14	6.20	5.50	10.43	1.05	40.6	5.9	1927
1	28	Nn72, P, K	2.91	2.76	0.35	0.48	0.11	0.08	4.20	5.90	7.98	1.10	47.4	6.0	1931
1	29	P, K	2.96	2.96	0.88	0.53	0.48	0.16	4.45	N D	9.46	1.30	53.0	6.1	1932
1	30	Ns24, P, K	1.31	1.31	0.31	0.33	0.15	0.11	6.60	7.71	8.81	0.90	25.0	5.3	1931
1	31	Ns48, P, K	0.73	0.38	0.33	0.38	0.11	0.10	8.10	8.34	9.40	1.30	13.8	4.96	1931
1	32	Ns72, P, K	0.45	0.45	0.59	0.27	0.18	0.14	8.70	8.65	10.33	0.75	15.5	4.5	1927
1	32	Ns72, P, K	0.75	0.65	0.31	0.38	0.07	0.07	8.80	8.40	10.28	0.70	14.5	4.7	1931
1	34	$CaCO_3$	17.10	11.60	0.49	0.38	0.07	0.05	0.00		12.59	43.60	100+	8.4	1931
1	34	$CaCO_3$	68.00	15.85	0.95	0.30	0.17	0.05	0.00		17.32	69.50	100+	8.2	1932
1	35	Nb30, Pb, K	5.11	5.11	1.57	0.56	0.21	0.10	1.95	N D	9.50	1.67	79.5	6.6	1932
1	36	None	4.84	3.84	0.86	0.29	0.12	0.12	2.60	3.80	7.83	1.85	66.8	6.2	1927
2	21	Nb72, P, K, Ca	5.82	5.82	0.89	0.45	0.13	0.06	0.89	N D	8.24	1.10	89.2	6.8	1932
2	30	Nb24, P, K, Ca	7.12	3.90	1.53	0.32	0.14	0.04	0.00	N D	5.93	1.03	100+	7.3	1932

TABLE 17—*Concluded*

TIER	PLOT	FERTILIZERS ALTERNATE YEARS	TOTAL Ca EXTRACTED	Ca	Mg	K	Na	NH_4	H TITRATION	H NH_4Ac	TOTAL	TOTAL CO_3	PER CENT SATURATION	pH	YEAR SAMPLED
2	31	Ns48, P, K, Ca	6.70	5.23	1.51	0.37	0.12	0.07	0.00	N D	7.30	2.87	100+	7.15	1932
2	32	Ns72, P, K, Ca	6.60	4.65	1.33	0.53	0.12	0.15	0.00	N D	6.78	2.80	100+	7.00	1932
3	1	None	4.42	3.57	1.68	0.30	0.11	0.04	2.00	N D	7.70	1.40	74.0	6.53	1932
3	2	Nb24	3.40	2.68	1.14	0.25	0.11	0.04	3.44	N D	7.66	1.50	55.1	5.8	1932
3	3	P	4.49	3.64	1.14	0.14	0.11	0.02	2.70	N D	7.75	1.45	62.7	6.2	1932
3	4	K	3.64	2.99	1.39	0.68	0.14	0.06	2.10	N D	7.36	1.45	71.5	6.5	1922
3	8	None	4.24	3.74	1.33	0.23	0.12	0.06	2.10	N D	7.58	1.15	72.3	6.5	1932

Nb24, etc. refer to dried blood equal to 24 pounds of N.
Nn and Ns refer to nitrate of soda and sulfate of ammonia.
P refers to superphosphate equivalent to 48 pounds P_2O_5. Previous to 1917 dissolved bone black was used in place of superphosphate.
Pb refers to ground bone, equivalent to 48 pounds P_2O_5.
K always refers to muriate of potash equal to 100 pounds K_2O.
M6, M8, and M-10 refer to 6, 8, and 10 tons manure.
On plot 34, two tons $CaCO_3$ on corn and wheat.
On plot 22 and 23, two tons CaO are applied to corn only.

In both correlations, with one or two exceptions a close relationship is shown to exist. When exchange hydrogen is determined by titrating the ammonium acetate extract it is found that soils with pH values of 7.00 are about 75 per cent saturated; when, however, direct titration is resorted to, it is found that soils 100 per cent saturated have pH values very close to 7.00. The writer favors the latter method. It should be mentioned however, that the determination of exchange hydrogen by titration of the ammonium acetate extract was not performed exactly as recommended by Schollenberger. The extraction was not carried out in the absence of air, which might account for higher results with this method than with direct titration of the soil. However, the writer has generally found that normal ammonium acetate becomes more, rather than less, alkaline on exposure to the atmosphere.

SUMMARY

The effect of cropping, with its crop removals, augmented leaching, organic decay, and erosion, is brought out by comparing the unfertilized plots with the adjacent grass strips. Cultivation has resulted in a small decrease of exchangeable calcium and magnesium without an increase in exchangeable hydrogen. The quantity of exchange ammonium in the grass strips is two to three times greater than in the check plots.

Barnyard manure caused an increase in total exchange capacity, the increase being mainly due to replaceable hydrogen and magnesium. The quantity of other ions is not changed.

On those plots which have received large amounts of lime, either as burnt lime or as limestone, ever since the field experiment was begun, the soils are saturated with calcium, a large quantity of calcium is present as carbonate, and the total exchange capacity is increased. Replaceable magnesium is also higher on these plots, but the other cations are unaffected. Within a few weeks after lime is applied, whether it be CaO or $CaCO_3$, the pH value becomes approximately 8.3 to 8.4. Immediately after liming with burnt lime the pH value is raised considerably above these values.

The continued use of a mixture of superphosphate and muriate of potash, when compared with the check plots, has resulted in an increase in total exchange capacity. This fertilizer combination has decreased the replaceable calcium and increased the hydrogen content. Magnesium is unaffected, but potassium is decidedly increased.

Superphosphate alone caused neither increase nor decrease in calcium but did increase exchange hydrogen. This fertilizer has resulted in a diminution of magnesium and potassium which is believed to be due to larger crop removals than on the check plots. Superphosphate increases soil acidity slightly.

When compared with superphosphate, ground bone is found to increase replaceable calcium and the degree of saturation and to raise the pH value of the soil.

Dried blood has resulted in marked loss of calcium and magnesium with corresponding increase in hydrogen. The amount of bases lost and of hydrogen gained is not directly proportional to the quantity of blood used. It is concluded that when soils become depleted of active bases the stronger acids may leach out as iron or alumina salts or as free acids.

The sodium of nitrate of soda was not adsorbed, and the quantity of other bases was not altered by the use of large amounts of nitrate of soda. Hydrogen was reduced and the total exchange capacity diminished by from 2 to 3 m.e.

As a result of the use of large amounts of sulfate of ammonia over a period of 50 years there has been a marked decrease of calcium and magnesium and a small loss of potassium. Hydrogen has replaced these ions so that now the most acid plots are only 15 per cent saturated. It is noteworthy that, although this salt has reduced the quantity of three bases, Ca, Mg, and K, the ill effects are apparently overcome by lime alone. It is pointed out that under field conditions it is not possible to determine, by calculation, how much lime is needed to counteract the acidity produced by an application of sulfate of ammonia.

Muriate of potash appears to have replaced calcium by potassium. Though there has been a loss of calcium there has been no gain in hydrogen and no appreciable change in pH value.

A comparison is made between the three most acid plots on tier 1, unlimed, and the corresponding three plots on tier 2, limed in 1921. This single application has restored the calcium and magnesium contents and the yields. Replaceable hydrogen has been practically eliminated, and the soils have been brought to approximately pH 7.00. Apparently no permanent injury was inflicted upon the soil as a result of being kept in such an acid condition for so long a time.

It is concluded that when fertilizer salts are used in sufficiently large amounts and for a sufficiently long period of time, they may, in some cases, produce measurable and significant effects upon the cation exchange picture of a soil. The differences so produced may have a profound influence upon the productivity of a soil.

Attention is called to the fact that errors in judgment may be as serious in interpreting a field experiment that has continued for a very long period as in interpreting one that has not continued long enough.

REFERENCES

(1) Aarnio, B. 1927 Influence of adsorbed ions on soil reaction. *Proc. First Internatl. Cong. Soil Sci.* 2: 65–76.

(2) Allison, F. E. 1931 The comparative effects of concentrated nitrogenous fertilizers on permanent soil acidity. *Jour. Amer. Soc. Agron.* 23: 878–908.

(3) Allison, F. E., Braham, J. M., and MacMurtrey, J. E. 1927 Field experiments with atmospheric nitrogenous fertilizers. U. S. Dept. Agr. Bul. 1180.

(4) Allison, F. E., and Cook, R. C. 1917 The effect of ammonium sulphate on soil acidity. *Soil Sci.* 3: 507–512.

(5) Andre, G. 1916 Displacement of potassium and phosphorus of certain rocks by some fertilizers. *Compt. Rend. Acad. Sci.* (Paris) 162: 133–136.

(6) BARBER, H. H., AND KOLTHOFF, I. M. 1928 A specific reagent for the rapid gravimetric determination of sodium. *Jour. Amer. Chem. Soc.* 50: 1625–1631.
(7) BARNETTE, R. M., AND HESTER, J. B. 1930 Influence of inorganic nitrogen compounds on reaction and replaceable bases of Norfolk sand. *Soil Sci.* 30: 431–437.
(8) BAVER, L. D. 1930 Relation of the amount and nature of exchangeable cations to the structure of a colloidal clay. *Soil Sci.* 30: 291–310.
(9) BRADFIELD, R. 1924 The importance of H-ion concentration control in physico-chemical studies of heavy soils. *Soil Sci.* 17: 411–412.
(10) BRADFIELD, R. 1927 The saturation capacity of colloidal clay soils. *Proc. First Internatl. Cong. Soil Sci. Misc. Papers.* 4, 5, 6: 858–868.
(11) BRAY, R. H. 1928 The quantitative and qualitative determination of replaceable sodium in alkali and non-alkali soils. *Jour. Amer. Soc. Agron.* 20: 1160.
(12) BURGESS, P. S. 1922 The reaction of soils in the field as influenced by the long continued use of fertilizer chemicals. R. I. Agr. Exp. Sta. Bul. 189.
(13) BURGESS, P. S. 1929 The so-called "build up" and "break-down" of soil zeolites as influenced by reaction. Univ. Ariz. Tech. Bul. 28.
(14) CHRISTENSEN, H. R., AND JENSEN, S. T. 1926 On the quantitative determination of lime requirement of soils. *Trans. Second Comn. Internatl. Soc. Soil Sci.* A: 94.
(15) CLARK, N. A., AND COLLINS, E. R. 1930 Equilibrium between soil and electrolytes and its influence upon some lime requirement methods. *Soil Sci.* 30: 417–425.
(16) CONREY, G. W., AND SCHOLLENBERGER, C. J. 1927 The effect of weathering on the exchangeable bases as shown in the Clermount silt loam profile. *Proc. First Internatl. Cong. Soil Sci.* 2: 227.
(17) CROWTHER, E. M. 1925 Studies on Soil Reaction: V. The depth distribution of reaction and flocculation in continuously manured soils. *Jour. Agr. Sci.* 15: 232–236.
(18) CROWTHER, E. M., AND BASU, J. K. 1931 Studies on soil reaction: VIII. The influence of fertilizers and lime on the replaceable bases of a light acid soil after fifty years of continuous cropping with barley and wheat. *Jour. Agr. Sci.* 21: 689–716.
(19) FUDGE, J. F. 1928 The influence of various nitrogenous fertilizers on the availability of phosphate and potassium. Ala. Polytech. Inst. Bul. 227.
(20) GEDROIZ, K. K. 1931 Exchangeable cations of the soil and the plant: I. Relation of plant to certain cations fully saturating the soil exchange capacity. *Soil Sci.* 32: 51–64.
(21) HALL, A. D., RUSSELL, E. J. 1927 The Book of the Rothamsted Experiments, p. 237. E. P. Dutton, New York.
(22) HARDY, F., AND LEWIS, A. H. 1929 A rapid electrometric method for measuring the lime requirement of soils. *Jour. Agr. Sci.* 19: 17.
(23) HUMFIELD, H. 1928 Electrodialysis of soils: III. Effect of different fertilizer treatments of soils on the bases and acids extracted by electro-dialysis. *Jour. Amer. Soc. Agron.* 20: 1141–1159.
(24) KAPPAN, H. 1926 Ober Zusammenhänge zwischen der Bodenaziditat und der physiologisch sauren Reaktion der Düngsmittel. *Trans. Second Comn. Internatl. Soc. Soil Sci.* 1926: 244–248.
(25) KAPPEN, H. 1927 The physiological reaction of fertilizers. *Amer. Fert.* 66: 41.
(26) KELLEY, W. P., AND CUMMINS, A. B. 1923 The formation of sodium carbonate in soils. Calif. Agr. Exp. Sta. Tech. Paper 3.
(27) LEMBERG, J. 1876 Über Silicatumivandlungen, *Ztschr. Deut. Geol. Gesell.* 28: 519–562.
(28) MACINTIRE, W. H. 1919 The carbonation of burnt lime in soils. *Soil Sci.* 7: 325–443.
(29) MAGISTAD, O. C., AND BREAZEALE, J. F. 1928 Base exchange in orthoclase. Ariz. Agr. Exp. Sta. Tech. Bul. 24.
(30) MARTIN, J. C. 1929 The effect of crop growth on the replaceable bases in some California soils. *Soil Sci.* 17: 123–136.

(31) MERKLE, F. G. 1928 The influence of fertilizer treatments on the content of exchangeable cations in Hagerstown silt loam. *Soil Sci.* 26: 377–383.

(32) MERKLE, F. G. 1932 Fiftieth anniversary of the Jordan soil fertility plots. *Penna. Agr. Exp. Sta. Tech. Bul.* 273: 29–34.

(33) METZGER, W. H. 1929 The effect of moisture content and cropping on exchangeable calcium and magnesium with particular reference to rice soils. *Soil Sci.* 27: 305–318.

(34) MILNE, G. 1929 The cobalt nitrite (volumetric) method of estimating potassium in soil extracts. *Jour. Agr. Sci.* 19: 541–552.

(35) PAGE, H. J. 1927 The relation between the state of saturation of the soil and its hydrogen ion concentration with special reference to the reaction of "physiologically acid" fertilizers. *Proc. First Internatl. Cong. Soil Sci.* (by title).

(36) PAGE, H. J., AND WILLIAMS, W. 1924 Studies on base exchange in Rothamsted soils. *Trans. Faraday Soc.* 1924: 573–585.

(37) PARKER, F. W. 1927 The determination of exchangeable hydrogen in soils. *Jour. Amer. Soc. Agron.* 21: 1030–1039.

(38) PARKER, F. W. 1927 Methods for determining the amount and avidity of exchange hydrogen in soils. *Proc. First Internatl. Cong. Soil Sci.* 2: 164–174.

(39) Pennsylvania Agricultural Experiment Station Annual Reports 1894, 1901–02, 1907–08, 1911–12, 1916–17, and Bulletins 146, 175, and 204.

(40) PIERRE, W. H. 1927 Buffer capacity of soils and its relation to the development of soil acidity from the use of sulphate of ammonia. *Jour. Amer. Soc. Agron.* 19: 332–350.

(41) PIERRE, W. H. 1928 Nitrogenous fertilizers and soil acidity: I. Effect of various nitrogenous fertilizers on soil reaction. *Jour. Amer. Soc. Agron.* 20: 254–269.

(42) PIERRE, W. H. 1928 Nitrogenous fertilizers and soil acidity: II. The use of fertilizer combinations, lime and basic slag in correcting the acidity formed by various nitrogenous fertilizers. *Jour. Amer. Soc. Agron.* 20: 270–279.

(43) PIERRE, W. H. 1931 Acidity produced by sulphate of ammonia. *Jour. Indus. and Engin. Chem.* 23: 1441.

(44) PIERRE, W. R., AND WORLEY, S. L. 1928 The buffer method and the determination of exchangeable hydrogen for estimating the amounts of lime required to bring soils to definite pH values. *Soil Sci.* 26: 363.

(45) RAVIKOVITCH, S. 1930 Exchangeable cations and lime requirement in differently fertilized soils. *Soil Sci.* 30: 79–95.

(46) SCHOLLENBERGER, C. J. 1927 Exchangeable hydrogen and soil reaction. *Science* 65: 552–553.

(47) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Effect of cropping with various fertilizers, manure and lime treatments upon the exchangeable bases in plot soils. *Soil Sci.* 29: 371–394.

(48) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Analytical methods in base exchange investigations in soils. *Soil Sci.* 30: 161–173.

(49) SHARP, L. T., AND HOAGLAND, D. R. 1916 Acidity and adsorption in soils as measured by the hydrogen electrode. *Jour. Agr. Res.* 7: 123–145.

(50) TIEDJENS, V. A., AND ROBBINS, W. R. 1931 The use of ammonia and nitrate nitrogen by certain crop plants. N. J. Agr. Exp. Sta. Bul. 526.

(51) WALKER, R. H., FIRKINS, B. J., AND BROWN, P. E. 1931 The measurement of the degree of saturation of soils with bases. Iowa Agr. Exp. Sta. Res. Bul. 139.

(52) WAY, J. T. 1852 On the power of soils to adsorb manure. *Jour. Roy. Agr. Soc.* 13: 123–143.

(53) WHITE, J. W. 1931 The effect of ammonium sulphate on soil reaction. *Jour. Amer. Soc. Agron.* 23: 871–877.

(54) WILSON, B. D. 1930 Exchangeable calcium and potassium in soils as affected by cropping and fertilizing. *Soil Sci.* 29: 91–100.

LIBRARY.

PHOSPHATE STUDIES: I. SOIL PENETRATION OF SOME ORGANIC AND INORGANIC PHOSPHATES[1]

V. E. SPENCER AND ROBERT STEWART

University of Nevada Agricultural Experiment Station

Received for publication August 18, 1933

I. INTRODUCTION

A differentiation of "available"

Much study has been made of the availability of various nutritive elements to plants. However, in the agronomic literature one finds considerable variation in the scope of the term *available*. Sometimes an author appears to mean by it only solubility in a given solvent, as measured in the laboratory. Again, it may apply to such nutrients as the plant extracts from a growth medium under defined conditions, as in the Neubauer test. In still other instances, it is meant to embrace all factors operating to insure the presence of assimilable nutrient in the plant's zone of absorption. This last, widest meaning appears to be the term's rightful scope, lexicologically.

Commonly, however, *available* is not used in its widest sense. One form of an element is said to be more "available" than another; "form," of course, referring to chemical composition. There is a definite tendency to associate availability with the chemical form in which a plant-food element exists. Recognition of this particular meaning is, in itself, entirely desirable; but use of the unqualified term *available* to designate it tends to confusion, especially in the light of recently increased attention to the effect of placement on the performance of applied fertilizers, for availability may depend upon *location* quite as much as upon *suitability*. So, to promote clarity in discussion of these factors, it seems very desirable to differentiate *available*.

In 1909, Fraps (3) defined four factors making for or against availability, and gave specific terms for each of them. Among these is *chemically available*, and this term seems better suited than any other to describe that factor of availability, based on the chemical form of a nutrient, which is at present almost invariably designated by the equivocal term *available*. Hence, following Fraps, we adopt the term *chemically available*, and favor its general use in speaking of the suitability possessed by a compound or ion, *per se*, which permits its satisfactory use as a nutrient by the plant.

Another term is needed to designate the type of availability dependent upon the location of the nutrient. In November, 1931, in a paper presented at the

[1] Published with the permission of the director, Nevada Agricultural Experiment Station.

American Society of Agronomy meeting in Chicago, we suggested the term *positional availability* to meet this need.

The following definitions of these terms seem adequate:

Chemical availability: The suitability possessed by element of plant food due to its combination in such chemical form that, when in contact with the feeding root, it is readily assimilated by the plant.

Positional availability: Perhaps this term may best be defined through definition of its antonym.

Positional unavailability: The lack of usefulness of a plant-food element, no matter how well its form of chemical combination may qualify it for assimilation by a plant, due to its being so situated in the soil that the roots of the plant cannot reach it. Weaver[2] defined this condition very aptly in saying that ". . . . too little attention has been paid to [assuring] the availability of nutrients to the root system itself, and the general belief is that anything that is put into the soil becomes available to the plant, as far as the plant coming into contact with it is concerned." In short, a *positionally unavailable* nutrient is one that is not within reach of the root system itself.

As for the unqualified term, we would define it as follows:

Available: Possessing both chemical and positional availability; implying the satisfactory condition of all the factors necessary to insure the assimilation of the nutrient by the plant.

Fraps included in his classification (3) "physically unavailable" nutrients, referring to chemically available compounds enclosed in "encrusting substance" which prevents contact between nutrient and root. At first thought, unavailability of the kind he there describes may appear to be identical with the positional unavailability to which we have called attention. Certainly it is true that if a soil particle containing a chemically available nutrient be surrounded by a shell of "encrusting substance" which precludes contact between the nutrient and the root hair, then a question of location is involved; the particle is not in a position to supply nutriment to the plant. But although position is the basis of both concepts, there is a distinct difference between them. If we interpret Fraps's meaning correctly, he refers to a soil particle which, although not in contact with any one of the roots of a plant, nevertheless lies *within* the zone of absorption by that plant's root system. In contrast with this condition, our positional unavailability depends on the fact that the nutrient lies *without* this zone of absorption. Figure 1 illustrates this difference.

CHEMICAL VS. POSITIONAL AVAILABILITY

That the place of fixation of applied phosphate may be an important factor in determining its availability seems probable. Reports by Midgley (13), Smalley (20), Hockensmith et al. (6), and others have shown decided superiority of deep over shallow placement of fertilizer. Truog (22) reported that for phosphate the "groove method of fertilization" gave better results than broadcasting. Truog explained this on the theory that when phosphate is broad-

[2] Weaver, John E. Private communication.

cast, it comes in contact with more of the soil's undesirable phosphate-fixing constituent (hydrated ferric oxide is suggested) than when localized in grooves, and hence in the former case more of the phosphate may be fixed "so tightly as to be largely unavailable to plants." Undoubtedly Truog's term *unavailable*,

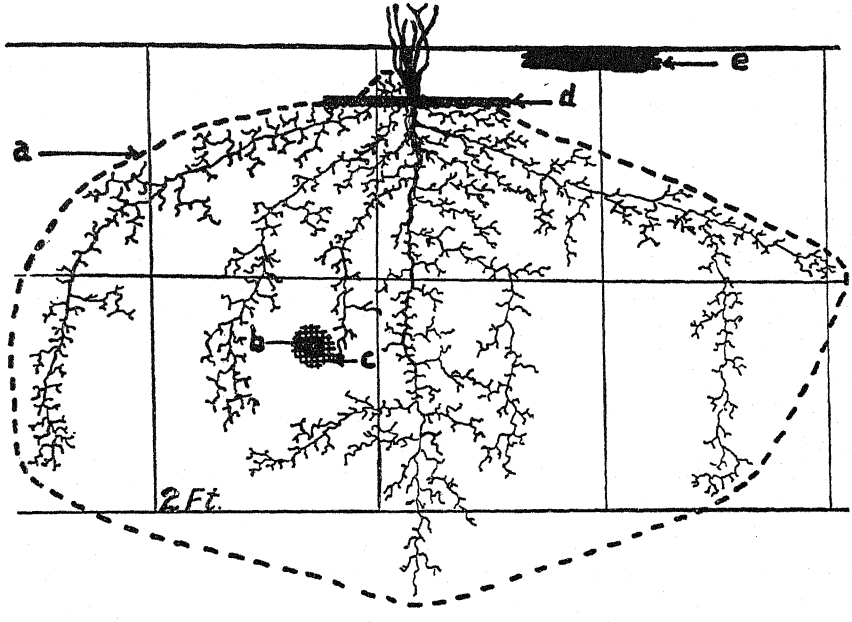


FIG. 1. DIAGRAM ILLUSTRATING THE MEANING OF THE PROPOSED TERM "POSITIONALLY UNAVAILABLE," AND HOW IT DIFFERS FROM THAT OF FRAPS'S TERM "PHYSICALLY UNAVAILABLE"

Root system after Weaver. By Courtesy of Professor Weaver and the publisher.

a represents, roughly, the boundary of the zone of absorption by the root system.

b illustrates "physically unavailable" nutrient as designated by Fraps (see text). *b* (the heavy black area) is a soil particle containing chemically available nutrient, but not in contact with the root because of the shell of "encrusting substance," *c* (the checkered area). The chemically available nutrient in *b*, therefore, Fraps classified as "physically unavailable." It lies within the zone of absorption, however, as contrasted with *e* and portions of *d*.

d represents phosphate applied in a band 4″ x 10″, $2\frac{3}{4}$″ below the surface. If this is fixed so that it moves downward little, some portion of it will remain outside the zone of absorption and thus be, according to our definition, positionally unavailable.

e represents phosphate fixed entirely outside the zone of absorption, and therefore positionally unavailable.

based as it is on fixation "so tightly," must be taken to mean *chemically unavailable* as we defined it in the foregoing. Thus his approval of the groove method seems to rest on the idea of avoiding chemical unavailability. The question arises, however, as to whether or not the groove method, in addition to localizing the phosphate, placed it deeper into the soil, as well.

On the other hand, Midgley (13) stated in favor of mixing the phosphate with the soil, his reason obviously being the necessity for more root-zone and less surface fixation; i.e., the achievement of greater positional availability. That he secured greater availability is apparent from his results; and it seems very probable that this was due to the positional, and not the chemical, factor. For if, as Truog suggested, the mixing incident to broadcasting is sufficient to render phosphate "unavailable" through tight fixation, then Midgley's success with his method of application, involving far more thorough mixing and dilution of the phosphate with the soil, can scarcely be explained on the basis of better chemical availability.

It appears to the authors that Truog's explanation (22) of the superiority of localized over broadcast fertilization, namely, that better "availability" (chemical availability) is insured by the former, may in some instances be less logical than one which postulates less positional availability for the latter. Phosphate broadcast on the surface and harrowed in is not placed very deep mechanically, nor can it go very deep via leaching if the soil is high in fixing power. Logically, then, one might expect it to have little positional availability in the current season of its application. Drouth conditions would still further reduce its positional availability; while optimum moisture supply near the surface might increase it somewhat, as Midgley found (13, p. 793) in the case of sudan grass, but to no such extent as would deeper placement.

When the phosphate is placed below the surface, the relative merits of localization and dispersion are more obscure because the situation is more complicated. It is no longer simply a case, in the main, of contact or lack of it between the feeding roots and the fixed nutrient. One important question is: Considering a given added phosphate and a given soil, what concentration of the one in the other is best from the standpoint of optimum availability and percentage utilization? Again we find in Midgley's work a pertinent indication. His results (13, p. 792, table 3, and p. 793, table 4) show, both for bluegrass in pot cultures and for sorghum and sudan grass in field plats, that 300 and 500 pounds per acre, respectively, of 20 per cent superphosphate mixed 3 inches deep was somewhat superior to the same amounts mixed 6 inches deep. For the 6-inch depth of application, the concentration of applied phosphate in the soil was theoretically half of that for the 3-inch depth. As the results were in favor of the shallower of the two placements, and since it is not probable that there was greater root activity in the surface than in the second 3-inch layer, it appears that lessened chemical availability, in line with Truog's theory, may have been responsible.

Thus it is possible that with some soils at least, and within certain limits, we may find two opposite trends accompanying dispersion of the added phosphate; (*a*) positional availability increasing with such dispersion because a greater portion of the fertilizer is thus distributed in the root zone, and (*b*) chemical availability decreasing because of the "tighter" fixation which may occur when the phosphate is thus diluted with the soil. Should this prove to be so, then,

for a given application (amount), the problem is to find the happy medium—that point at which the curve of increasing positional availability crosses the curve of decreasing chemical availability. A thorough study of this question would, we believe, be worth while; apparently few data bearing on it are on record.

SHOULD CHEMICALLY AVAILABLE NUTRIENT BE LOCALIZED OR DISPERSED WITHIN THE ROOT ZONE?

Would a phosphatic fertilizer not rendered chemically unavailable on dispersion throughout the root zone, function more efficiently when so dispersed than when concentrated in a small portion of the root zone? This question involves what Truog (22) has referred to as "the modern cafeteria idea" with respect to the feeding of plants. He has stated that "Plants seem to be able to adjust themselves to feed locally for one thing here and something else there." In view of the great number of instances of crop increase due to superphosphate application, and of the fact that in many of these instances the applied nutrient must have been localized within a comparatively small portion of the root zone, some measure of correctness must be recognized in this viewpoint. However, is the plant able to do as well, where the nutrient is available to a part, only, of its root system, as it would do with an optimum concentration of the nutrient existing uniformly throughout its entire root zone? Jensen (8), in reporting the failure of phosphate (146 pounds per acre of 4–10–6 fertilizer hill-dropped for corn) to penetrate appreciably beyond its original position, expressed wonder that such a method of application does not result in more failures to produce increased yields. Probably some such failures which have been observed could have been avoided had there been better distribution of the phosphate. Smalley (20, p. 37) also, while admitting the undoubted worth of present methods of application, relevently asked if they are the best possible, or if they would be so if the rate of application should be doubled. For instance, it is interesting to speculate on what Midgley's results might have been, in the case of his placements of phosphate throughout the 6-inch depth, had he had the same concentration of the applied nutrient in that 6-inch layer as he had when he mixed the same amount to the 3-inch depth only; in other words, had he doubled the amount applied when he doubled the depth of mixing.

We have mentioned "tight" fixation, assuming that it results in chemical unavailability, as a possible explanation of the lesser yield increases Midgley obtained with some crops for the 6-inch depth of mixing, as compared with the 3-inch depth. But corn, in the same experiment, did vastly better with the 6-inch placement, just the reverse of the other crops. How may this be explained other than on the basis of better positional availability? But if this explanation be taken as valid, then the "cafeteria" theory of plant feeding becomes less convincing, for if it be assumed that the phosphate mixed with the surface 3-inch layer was sufficiently within the plants' feeding range, then there was ample opportunity for them to secure their phosphorus on the "cafe-

teria" plan, and also there was the assumed added advantage of less tight fixation. Yet the corn did better with deeper placement and greater dispersion of the fertilizer, even though this involved more mixing and dilution with the soil.

The same reasoning applies to Smalley's results (20) with cotton; the greater yield for the same amount of fertilizer in two bands, as compared with one, argues not only on the side of deeper placement of the nutrient, but also in favor of its more extensive dispersion in the root zone.

It is recognized, of course, that the experiments cited are too few to be conclusive. But they are distinctly relevant to the questions we have raised regarding the chemical and positional factors of availability; and their results indicate a need for much more investigation of these questions, as well as that of the extent to which the "cafeteria" theory of plant feeding holds.

For adequate field investigations of these questions a means of obtaining deep and uniform distribution of applied phosphorus is essential. Dyer (2) observed that in soil manured for 50 years phosphorus had penetrated deeper than where superphosphate had been applied. Stephenson and Chapman (21) report finding a similar slow effect of manure. Plainly, however, the prospect of waiting for many years to accomplish deep distribution of phosphorus is not conducive to the inauguration of experiments designed to test the effect of such distribution. Also, the several inseparable variables inherent in such a method disqualify it. As for mechanical placement of the phosphorus deeply and uniformly, this, too, is objectionable, both from the standpoints of costliness and of the variables involved. Thus, without a phosphate able to penetrate the soil readily, it has been impossible adequately to determine the effect of applied phosphate distributed uniformly below the plowed depth. It is our hope that the work reported in this paper, revealing the application of an important chemical principle to the problem of lessening phosphate fixation, may lead to a feasible method of placing phosphate appreciably below the plow line, so that field investigation of the foregoing questions may be made possible.

WHERE ARE THE ROOTS?

Apparently for a long time the general opinion has been that root systems of our field crops are essentially shallow. Van Alstine (23, p. 283) stated that by far the most feeding is done in the surface 7 inches of soil. Laird (9) found that the root systems of several sod-forming grasses were larger and deeper than are "ordinarily expected."

Millar (14) found that the root systems of young corn plants (averaging about 9 inches in height) were usually from 3 to 4½ inches below the surface, depending on the soil type, at a point 6 inches from the plant; and that 9 inches away the root depth ranged from 4 to 5 inches. Millar's study was concerned with the question of optimum placement of fertilizer for giving the young plant "early" benefit while at the same time avoiding damage to the

seedling. But is early benefit, desirable as it is, *all* that we should require of a fertilizer? The answer, of course, is no. Then comes the question: Is early benefit all, or mainly, what we are getting from an applied nutrient which is fixed in a very restricted portion of the root zone, near the surface?

The extensive and admirable studies of Weaver, on root development, have revealed information of primary importance in the consideration of the fertilizer placement question. He has shown (24) that instead of being shallow as was commonly supposed, the roots of cultivated plants are deeply seated and absorb both water and nutrients in relatively large quantities from depths even below 2 feet. Particularly, he states that this deep absorption occurs in the latter, more critical stages of the plants' development. This may be due in some measure to other facts he mentions; namely, that absorption is practically limited to the root-hair zone, occurring on the younger portions of the roots, and that this zone migrates as the roots grow further into the soil (24, p. 44).

Other pertinent points brought out by Weaver (24, p. 57) are, that when roots encounter a fertilized soil layer there are marked increases in their number and branching; and that in such a case, normal development of the root system below this layer is retarded. It is conceivable, therefore, that should the fertilized layer be too near the surface, under drouth conditions the plant's quest for moisture might compel the roots to forage deeper, at the expense of securing the maximum benefit from this layer. Or, failure thus to react would leave the plant unusually vulnerable to the drouth. Mann (11, p. 58) observed that "especially in seasons of drouth is deep fertility a factor;" and Midgley (13, p. 793) attributed the efficacy of broadcast superphosphate, for sudan grass, to the unusually good moisture condition close to the surface due to shading by the grass.

It is well established that root systems, even within a given species or variety, vary widely depending upon environmental factors. Weaver (24, p. 61) mentions this fact regarding many cultivated crops, as well as fruit trees; and with respect to the latter, such variation is clearly indicated by Gardner, Bradford, and Hooker (4). In some situations, maximum efficiency of applied nutrients which were fixed by the soil may have been obtained. However, we are inclined to suspect that instances of such efficiency are relatively rare. Roots as a rule forage far deeper than it has been feasible to place phosphatic and potassic fertilizers, and it is therefore essential that, as Weaver (24) and Stephenson and Chapman (21) have aptly emphasized, a thorough study be made of possible means of obtaining deep placement, and of its effects in crop production.

THE PRESENT PROBLEM

The fundamental aim in the work herein reported was to discover some means of attaining more extensive distribution of applied phosphate in the soil than is feasible at present. This objective is not new, although it appears to have lain in the discard for nearly a century. As a background for the present work, it is worth while to mention very briefly some past efforts in this direction.

These began at least as early as 1774, when Anthony St. Leger experimented with ground and unground bones, to ascertain their respective merits as sources of *oil*, then supposed to be the food of plants. A brief account of his results appears in Hopkins' book (7) on soil fertility. The better dispersion of the bones in the soil, as a result of grinding, naturally resulted in their greatly increased efficiency as fertilizer.

That Liebig, also, about 1840, had in mind only the better dispersion of the bone substance in the soil, when he originated the practice of dissolving bones in sulfuric acid and applying them in this form, is indicated by his statement (10):

> The most easy and practical mode of effecting their division is to pour over the bones, in a state of fine powder, half of their weight of sulfuric acid, diluted with three or four parts of water; and after they have been digested for some time to add 100 parts of water and sprinkle this mixture over the field before the plow. In a few seconds the free acids unite with the bases contained in the earth and a neutral salt is formed in a very fine state of division. Experiments have distinctly shown that neither corn nor kitchen garden plants suffer injurious effects in consequence, but that, on the contrary, they thrive with much vigour.

Evidently Liebig considered the value of acidulation to lie in the accomplishment of fine division of the bones, and their better distribution in the soil, rather than in any improvement of their efficiency due to change in chemical form; for in addition to his initial statement of division as the thing to be effected, he further took pains to point out the absence of any *harmful* consequence of the acid treatment. Indeed, it seems reasonable to believe he tacitly accepted the idea that after acidulation, and subsequent precipitation in the soil, the bones now had essentially the same chemical form they had before treatment with sulfuric acid. Thus Liebig's important suggestion, out of which has grown a vast superphosphate industry, undoubtedly was the result of his quest for increased availability of the positional, and not the chemical, kind.

However, from Liebig's time down to the present it appears to have been generally taken for granted that the problem of causing phosphate to permeate the soil was satisfactorily solved; this in the face of the known fact of phosphate fixation. Seemingly, at least prior to the last few years, the lion's share of the attention of agriculturists has centered on the initial water solubility of superphosphate, assumed to result in an entirely satisfactory distribution of the nutrient throughout the soil, rather than on possible effects depending on its place of fixation. Then, a growing recognition that, after all, the long-assumed ideal placement of applied phosphate probably was more imaginary than real, may have helped to bring about placement experiments. The most extensive of these have been conducted by the Joint Committee on Fertilizer Application (17, 22). In them, the chief aim seems to have been the localization of the applied fertilizer in the most favorable position in the soil; and the mode of attack has been mechanical placement. With respect to phosphate,

the localization feature has been favored on the assumption that it minimizes undesirable fixation and thus promotes greater chemical availability, as already mentioned in the discussion of Truog's theory.

In contrast to this concept of increasing chemical availability through localization of the phosphate, our work rests on the idea of increasing positional availability through wider dispersion of the phosphate—that is to say, its deeper premeation of the soil. Thus our objective is, in kind, identical with that of St. Leger and Liebig. We seek to extend the scope of phosphate dispersion so that it will be effective below the plow line, a result which they did not accomplish.

Plan of attack

The observation does not appear to have been made previously[3] that some chemical adjustment of the phosphorus-carrying molecule might be found which would lessen the fixation and thus result in more extensive permeation of the soil. Before we began experimental work on the problem, we had reached the conclusion that a study of this possibility was a logical direction in which to work toward the objective; and that such a study would be very desirable in connection with the question of securing deep placement of phosphate.

Since, no matter what soil constituents are responsible for phosphate fixation, or what the compounds resulting from it, the basic fact is that these compounds are essentially insoluble, the problem was to find some "solubilizing" agent which could be incorporated in the phosphorus-carrying molecule so that the combined phosphorus, whether or not it kept its original chemical form after application to and possible reaction with the soil, would retain its water solubility long enough to permit it to penetrate deeper into the soil.

Such a "solubilizing" agent readily suggested itself. The effect of the hydroxyl group in promoting water solubility of organic compounds is well known. We therefore took as a working hypothesis the idea that a compound in which the phosphate radical is combined with an organic radical, the latter having one or more hydroxyls, should be able to escape fixation on account of the solubility effect. A general formula for such compounds would be $R(OH)_x - (OPO_3M_y)_z$; and a specific example, $C_3H_5(OH)_2 - OPO_3Ca$, which is the calcium mono-orthophosphate of glycerol. Another specific example would be potassium sorbityl di-orthophosphate, $C_6H_8(OH)_4 - (OPO_3K_2)_2$.

EXPERIMENTAL

A preliminary trial with calcium glycerophosphate convinced us of the correctness of the aforementioned hypothesis as a basis for further study. A 6-

[3] Since we began work on the soil-penetrating properties of organo-phosphates, Midgley, to whose paper reference has already been made, has in that paper pointed out that di-sodium phosphate is fixed less readily than some other inorganic phosphates. We have used pure di-sodium phosphate in percolation trials, and the results are given in table 1.

These began at least as early as 1774, when Anthony St. Leger experimented with ground and unground bones, to ascertain their respective merits as sources of *oil*, then supposed to be the food of plants. A brief account of his results appears in Hopkins' book (7) on soil fertility. The better dispersion of the bones in the soil, as a result of grinding, naturally resulted in their greatly increased efficiency as fertilizer.

That Liebig, also, about 1840, had in mind only the better dispersion of the bone substance in the soil, when he originated the practice of dissolving bones in sulfuric acid and applying them in this form, is indicated by his statement (10):

> The most easy and practical mode of effecting their division is to pour over the bones, in a state of fine powder, half of their weight of sulfuric acid, diluted with three or four parts of water; and after they have been digested for some time to add 100 parts of water and sprinkle this mixture over the field before the plow. In a few seconds the free acids unite with the bases contained in the earth and a neutral salt is formed in a very fine state of division. Experiments have distinctly shown that neither corn nor kitchen garden plants suffer injurious effects in consequence, but that, on the contrary, they thrive with much vigour.

Evidently Liebig considered the value of acidulation to lie in the accomplishment of fine division of the bones, and their better distribution in the soil, rather than in any improvement of their efficiency due to change in chemical form; for in addition to his initial statement of division as the thing to be effected, he further took pains to point out the absence of any *harmful* consequence of the acid treatment. Indeed, it seems reasonable to believe he tacitly accepted the idea that after acidulation, and subsequent precipitation in the soil, the bones now had essentially the same chemical form they had before treatment with sulfuric acid. Thus Liebig's important suggestion, out of which has grown a vast superphosphate industry, undoubtedly was the result of his quest for increased availability of the positional, and not the chemical, kind.

However, from Liebig's time down to the present it appears to have been generally taken for granted that the problem of causing phosphate to permeate the soil was satisfactorily solved; this in the face of the known fact of phosphate fixation. Seemingly, at least prior to the last few years, the lion's share of the attention of agriculturists has centered on the initial water solubility of superphosphate, assumed to result in an entirely satisfactory distribution of the nutrient throughout the soil, rather than on possible effects depending on its place of fixation. Then, a growing recognition that, after all, the long-assumed ideal placement of applied phosphate probably was more imaginary than real, may have helped to bring about placement experiments. The most extensive of these have been conducted by the Joint Committee on Fertilizer Application (17, 22). In them, the chief aim seems to have been the localization of the applied fertilizer in the most favorable position in the soil; and the mode of attack has been mechanical placement. With respect to phosphate,

the localization feature has been favored on the assumption that it minimizes undesirable fixation and thus promotes greater chemical availability, as already mentioned in the discussion of Truog's theory.

In contrast to this concept of increasing chemical availability through localization of the phosphate, our work rests on the idea of increasing positional availability through wider dispersion of the phosphate—that is to say, its deeper premeation of the soil. Thus our objective is, in kind, identical with that of St. Leger and Liebig. We seek to extend the scope of phosphate dispersion so that it will be effective below the plow line, a result which they did not accomplish.

Plan of attack

The observation does not appear to have been made previously[3] that some chemical adjustment of the phosphorus-carrying molecule might be found which would lessen the fixation and thus result in more extensive permeation of the soil. Before we began experimental work on the problem, we had reached the conclusion that a study of this possibility was a logical direction in which to work toward the objective; and that such a study would be very desirable in connection with the question of securing deep placement of phosphate.

Since, no matter what soil constituents are responsible for phosphate fixation, or what the compounds resulting from it, the basic fact is that these compounds are essentially insoluble, the problem was to find some "solubilizing" agent which could be incorporated in the phosphorus-carrying molecule so that the combined phosphorus, whether or not it kept its original chemical form after application to and possible reaction with the soil, would retain its water solubility long enough to permit it to penetrate deeper into the soil.

Such a "solubilizing" agent readily suggested itself. The effect of the hydroxyl group in promoting water solubility of organic compounds is well known. We therefore took as a working hypothesis the idea that a compound in which the phosphate radical is combined with an organic radical, the latter having one or more hydroxyls, should be able to escape fixation on account of the solubility effect. A general formula for such compounds would be $R(OH)_x - (OPO_3M_y)_z$; and a specific example, $C_3H_5(OH)_2 - OPO_3Ca$, which is the calcium mono-orthophosphate of glycerol. Another specific example would be potassium sorbityl di-orthophosphate, $C_6H_8(OH)_4 - (OPO_3K_2)_2$.

EXPERIMENTAL

A preliminary trial with calcium glycerophosphate convinced us of the correctness of the aforementioned hypothesis as a basis for further study. A 6-

[3] Since we began work on the soil-penetrating properties of organo-phosphates, Midgley, to whose paper reference has already been made, has in that paper pointed out that di-sodium phosphate is fixed less readily than some other inorganic phosphates. We have used pure di-sodium phosphate in percolation trials, and the results are given in table 1.

inch layer of highly calcareous soil having high fixing power for phosphate, classified by the U. S. Bureau of Soils (1) as Las Vegas Loam, from southern Nevada, fixed an appreciable quantity of pure monocalcium phosphate, applied in solution, so that only a trace of phosphorus was found in the filtrate. In contrast with this, under the same conditions, and with the same amount of phosphorus applied, much phosphorus passed through the soil and was detected in the filtrate when calcium glycerophosphate was the substance added.

In order further to test the hypothesis, we extended our experiments to other organic phosphates of the same type; specifically, compounds resulting from the phosphorylation of ethylene glycol, glucose, and sorbitol. Along with the organics, several inorganic phosphorus carriers were examined for their ability to pass through the soil. All were tried under exactly the same conditions.

Phosphorus-carrying substances used in penetration tests

Inorganic.—Anaconda Treble Superphosphate, 45 per cent "available" P_2O_5, from Anaconda Copper Mining Company, Anaconda, Montana.

Ammo-phos B, 20 per cent "available" P_2O_5, from American Cyanamid Company, New York, N. Y.

Di-sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, Analytical Reagent grade, from Mallinckrodt Chemical Works, St. Louis, Missouri. The salt was assumed to be pure.

Metaphosphoric acid, glacial, sticks, from Eimer and Amend, New York, N. Y. Our analysis of this acid, as it came from the bottle, gave 32.59 per cent total phosphorus, whereas the theoretical value for the pure acid is 38.76 per cent.

Organic.—Calcium glycerophosphate, U. S. P., powder, from Eimer and Amend, New York. The salt gave no test for inorganic phosphorus, and for the purpose of this experiment was assumed to be pure. It is the monophosphate.

Calcium glucose-3-mono-orthophosphate. This was prepared from the basic barium salt, the latter being prepared by the method of Raymond and Levene (16). Treatment of the dissolved barium salt with calcium sulfate, followed by centrifugation, evaporation under reduced pressure, and precipitation with 95 per cent alcohol, gave the calcium salt of the organo-phosphate somewhat contaminated with calcium sulfate. The material gave no test for inorganic phosphorus. Its phosphorus content was 7.01 per cent.

Calcium glycol mono-orthophosphate. This salt was prepared as follows: 52 gm. of glycol (1.67 mol.) and 40 gm. of glacial metaphosphoric acid (1 mol.) were heated under an air condenser for $3\frac{1}{2}$ hrs. The maximum temperature reached was 193°C. The cooled mass was dissolved in cold water and a slight black residue filtered off. To the filtrate was added concentrated calcium chloride solution in excess, then an excess of solid calcium hydroxide, with

phenolphthalein indicator. After standing over night the mixture was filtered and the precipitate washed well with cold water. CO_2 was passed through the filtrate until the pink color was discharged. The mixture was then boiled for 10 minutes and filtered to remove calcium carbonate. This filtrate was concentrated to small volume, then four volumes of alcohol were added, and the precipitate filtered off and washed with 80 per cent alcohol. After recrystallization twice from water the product, pure white and crystalline, gave the following analyses:

0.1000 gm. substance: 0.0601 gm. $Mg_2P_2O_7$
0.1000 gm. substance: 0.0311 gm. CaO
$C_2H_5O_5PCa$. Calculated, P 17.30, Ca 22.24
Found, P 16.96, Ca 22.23

Calcium sorbityl mono-orthophosphate. The preparation of this compound was similar to that of the glycol phosphate. To 10 gm. of sorbitol[4] dissolved in a small quantity of water 10 gm. of glacial metaphosphoric acid was added. The mixture was heated in a porcelain dish on the steam bath overnight, during which time evaporation reduced it to a thick syrup. It was then heated over a free flame for 10 minutes, with care to prevent charring. The cooled mass was dissolved in cold water. From here on through the precipitation with alcohol the procedure was the same as that in the case of the glycol phosphate. The white product was dissolved in a minimum quantity of water and reprecipitated with alcohol. Subsequent purification consisted in dissolving in water, evaporating to dryness, redissolving in water, filtering, and again evaporating to dryness; this was repeated until all of the material readily passed into solution completely with no murkiness. The substance gave the following analyses:

0.1000 gm. substance: 0.0391 gm. $Mg_2P_2O_7$
0.1000 gm. substance: 8.675 cc. of 0.08385 N $KMnO_4$ sol.
$C_6H_{13}O_9PCa$. Calculated, P 10.34, Ca 13.35
Found, P 10.89, Ca 14.48

Of these organic phosphates, the glycol compound is least soluble in water, the order of increasing solubility being: calcium glycol phosphate, calcium glycerophosphate, and then the two others, calcium glucose phosphate and calcium sorbityl phosphate, which are both very soluble.

METHOD OF TESTING THE PHOSPHATES FOR SOIL PENETRATION

In the penetration tests, cylindrical glass percolator tubes, having an average internal diameter of 1.72 inches, were used. Thus the area of each soil column was 0.3725×10^{-6} acre. The soil used was the Las Vegas loam

[4] The sorbitol used in this investigation was kindly furnished by the Experimental Station of E. I. du Pont de Nemours & Co., Wilmington, Delaware. For this donation the authors make grateful acknowledgment.

mentioned above. In the bottom of each percolator a perforated porcelain disc was placed, and on this a pad of fine glass wool. On this pad, 405 gm. of air-dry soil, ground to pass a 3-mm. sieve, was placed, and over the levelled surface of this soil column the powdered phosphate was sprinkled evenly; then another pad of glass wool was put on top to prevent the formation of a suspension of fine soil on addition of the water.

Identical amounts of the element phosphorus were applied in all cases; the rate was equivalent to an application of 500 pounds of treble superphosphate per acre.

Each trial was run in duplicate. In all cases the results from duplicates agreed closely, and the figures given in the second column of table 1 are averages.

Duplicate blank percolations were run on the untreated soil, and the native

TABLE 1

Penetration of soil by various inorganic and organic phosphates

FORM OF PHOSPHORUS ADDED TO SURFACE OF SOIL	PHOSPHORUS, POUNDS PER ACRE, FOUND IN LEACHATE (LESS NATIVE PHOSPHORUS)	PER CENT OF ADDED PHOSPHORUS PASSING THROUGH SOIL
Inorganic phosphates		
Treble superphosphate	0.66	0.67
Metaphosphoric acid, glacial	4.21	4.28
Ammo-Phos B	6.19	6.30
Di-sodium phosphate	11.31	11.51
Organic phosphates		
Ca glycerophosphate	73.73	75.01
Ca glycol phosphate	77.78	79.13
Ca sorbityl phosphate	88.43	89.97
Ca glucose phosphate	93.20	94.82

phosphorus leached was subtracted from the total phosphorus found in the leachates from the treated soils.

With the treated soil in place in the percolator, water was added, and when the soil was just saturated so that percolation began, the column of water above it was adjusted to a depth of 8 inches. At 24-hour intervals, two more leachings were made in the same manner. Total phosphorus was determined in the leachates, after evaporation and decomposition by igniting with calcium nitrate, by the method given on page 3, second edition of "Official and Tentative Methods of Analysis" of the Association of Official Agricultural Chemists.

Table 1 gives the results of the percolation tests. The amount of irrigation was uniform throughout, and equalled 24 acre inches. In all percolators, the depth of soil (Las Vegas loam) was 7 inches. In each case, phosphorus (the element) was added at the rate of 98.29 pounds per acre.

DISCUSSION

The results bear out the hypothesis on which the work was begun and demonstrate the possibility of achieving greatly increased permeation of the soil by phosphate. This, in turn, may make it possible to determine whether or not applied phosphate, if more deeply dispersed in the soil than is now feasible, would be more efficient in supplying the needs of crops which forage appreciably below the plow line. While the results may be of special interest in consideration of orchard fertilization, it is felt that they may be of value also in contributing to possible improvement of phosphate placement for many of the common field crops.

The aforementioned observation by Dyer (2), and again by Stephenson and Chapman (21), that manure is in some way associated with deeper penetration of phosphate, is of interest in the light of the foregoing results. Possibly the phosphorus which had descended deeper than usual, which they noted, had existed in organic forms in the manure; decomposition of these might result in still other organic phosphates, similar in type to those given in table 1, having the soil-penetrating power. Another possibility is that during the decomposition of manure or other organic matter in the soil, fermentation may produce organic phosphates of the aforementioned type. Martin (12) reported the finding by Harden and Young that hexosephosphate is formed during the conversion of hexoses to alcohol and CO_2 by fermentation. Whether or not such phosphates are produced in the soil is not known to the authors, but there seems to be the possibility; the subject warrants investigation, as does also the question of the chemical forms in which phosphorus exists in manure.

Whatever the way in which manure increases phosphate penetration, the enhancement is but slight; either the penetrating phosphate is contained in or formed by the manure in small amount, or, if in appreciable amount, it is largely decomposed, and rather quickly, back into a fixable form. Otherwise there would be more extensive and more rapid permeation of the soil by phosphate than has been observed, and much more phosphorus in drainage waters than has been found there.

The question of the chemical availability of organic phosphates is a pertinent one. Some investigators have reported indications that organic phosphate they encountered in soil extracts is not "available" to plants (15, 18); others have found certain organic phosphates to be readily "available" (5, 19, 25). There are various forms of organic phosphate, and it is quite conceivable that some are chemically available and some are not. Then too, a further consideration presents itself: Is any organic phosphate, as such, absorbed by the plant, or must it first decompose so that the phosphorus becomes inorganic before entering the plant? We know of no investigation which has answered this question, and have planned experiments which we hope will help to decide it.

We have done some work on the chemical availability of the phosphorus in the penetrating type of phosphate reported. In pot cultures calcium glycero-

phosphate and one of our preparations, a crude phosphate of sorbitol, have proved to be very satisfactory sources of phosphorus for plant growth. The phosphates of glycol, sorbitol, and glucose given in table 1 are now being used in such trials. The results of our study of the chemical availability of phosphorus in compounds of this type will be presented in a subsequent paper.

Referring again to the penetration feature, our result for di-sodium phosphate, given in table 1, confirms Midgley's finding (13, p. 795) that phosphorus applied in this form penetrates the soil more readily than that applied as superphosphate or Ammo-Phos B.

SUMMARY

Since it is desirable to distinguish between (*a*) the "availability" of an element due to the suitability of its chemical form for plant nutrition, and (*b*) the "availability" of that element due to its being situated in the soil where the plant's roots can reach it, the term *available* has been differentiated into *chemically available* and *positionally available*. The unqualified term is reserved for the case wherein it is wished to denote collectively all factors which operate to insure the presence of assimilable nutrient within the plant's zone of absorption.

Brief discussion is given to the question of chemical vs. positional availability, with respect to the placement of phosphatic fertilizer; and to the location of crops' feeding roots.

The objective in the experimental work was to find a phosphate form having greater soil-penetrating power than the common phosphate carriers. The results show that phosphorus in organic phosphates of the type formula $R(OH)_x(OPO_3M_y)_z$ escapes, to a marked degree, the fixation which occurs to phosphorus applied in some inorganic forms.

REFERENCES

(1) CARPENTER, E. J., AND YOUNGS, F. O. 1926 Soil Survey of Las Vegas Area, Nevada. U. S. Dept. Agr. Bur. Soils. Advance Sheets—Field Operations of the Bureau of Soils, 1923. Govt. Printing Office, Washington, D. C.

(2) DYER, BERNARD 1902 Results of investigations on the Rothamsted soils. *U. S. Dept. Agr. Off. Exp. Sta. Bul.* 106, p. 112.

(3) FRAPS, G. S. 1909 Active phosphoric acid and its relation to the needs of the soil for phosphoric acid in pot experiments. Tex. Agr. Exp. Sta. Bul. 126.

(4) GARDNER, V. R., BRADFORD, F. C., AND HOOKER, H. D. 1922 The Fundamentals of Fruit Production, ed. 1, p. 54–64. McGraw-Hill Book Co., Inc., New York.

(5) HECK, A. F., AND WHITING, A. L. 1927 The assimilation of phosphorus from phytin by red clover. *Soil Sci.* 24: 17–29.

(6) HOCKENSMITH, R. D., GARDNER, ROBERT, AND KEZER, ALVIN 1933 The effect of depth of placement on the availability of superphosphate in calcareous soils. *Soil Sci.* 36: 35.

(7) HOPKINS, C. G. 1910 Soil Fertility and Permanent Agriculture, ed. 2, p. 305–306, Ginn and Co., Boston.

(8) JENSEN, OVE F. 1929 Movement of fertilizer salts in the soil. *Jour. Amer. Soc. Agron.* 21: 1113.

(9) LAIRD, A. S. 1930 A study of the root systems of some important sod-forming grasses. *Fla. Agr. Exp. Sta. Bul.* 211, p. 23.

(10) LIEBIG, JUSTUS VON 1840 Die Chemie in ihrer Anwendung auf Agrikultur und Physiologie.

(11) MANN, FRANK I. 1922 Newer problems in soil treatment. "Illinois Agricultural Policy," the report of a conference at the University of Illinois, Jan. 26–27, 1922, p. 56–60. Published by the University of Illinois.

(12) MARTIN, GEOFFREY 1917 Industrial and Manufacturing Chemistry. Part I. Organic. Ed. 3, p. 222. D. Appleton and Company, New York.

(13) MIDGLEY, A. R. 1931 The movement and fixation of phosphates in relation to permanent pasture fertilization. *Jour. Amer. Soc. Agron.* 23: 788–799.

(14) MILLAR, C. E. 1930 Root systems of young corn plants in relation to fertilizer applications. *Jour. Amer. Soc. Agron.* 22: 868–873.

(15) PIERRE, W. H., AND PARKER, F. W. 1927 Soil phosphorus studies: II. The concentration of organic and inorganic phosphorus in the soil solution and soil extracts and the availability of the organic phosphorus to plants. *Soil Sci.* 24: 119.

(16) RAYMOND, A. L., AND LEVENE, P. A. 1929 Synthetic hexosephosphates and their phenylhydrazine derivatives. *Jour. Biol. Chem.* 83: 619–630.

(17) SALTER, R. M. 1932 Recommendations of the Joint Committee on Fertilizer Application, November, 1932. *Jour. Amer. Soc. Agron.* 24: 995–1000.

(18) SCHOLLENBERGER, C. J. 1920 Organic phosphorus content of Ohio soils. *Soil Sci.* 10: 140.

(19) SCHREINER, O., AND SKINNER, J. J. 1912 Nitrogenous soil constituents and their bearing on soil fertility. U. S. Dept. Agr. Bur. Soils Bul. 87.

(20) SMALLEY, H. R. 1931 Research and demonstrations—the foundation of progress. *Proc. Seventh Ann. Conv. Natl. Fert. Assoc.*, p. 38. 616 Investment Bldg., Washington, D. C.

(21) STEPHENSON, R. E., AND CHAPMAN, H. D. 1931 Phosphate penetration in field soils. *Jour. Amer. Soc. Agron.* 23: 759–770.

(22) TRUOG, EMIL 1929 Problems in methods of applying fertilizers. *Amer. Fert.*, Dec. 21, 1929. Ware Bros. Co., Publishers, Philadelphia, Pa.

(23) VAN ALSTINE, E. 1918 The movement of plant-food within the soil. *Soil Sci.* 6: 281–308.

(24) WEAVER, JOHN E. 1926 Root Development of Field Crops, ed. 1, p. 53–91. McGraw-Hill Book Co., Inc., New York.

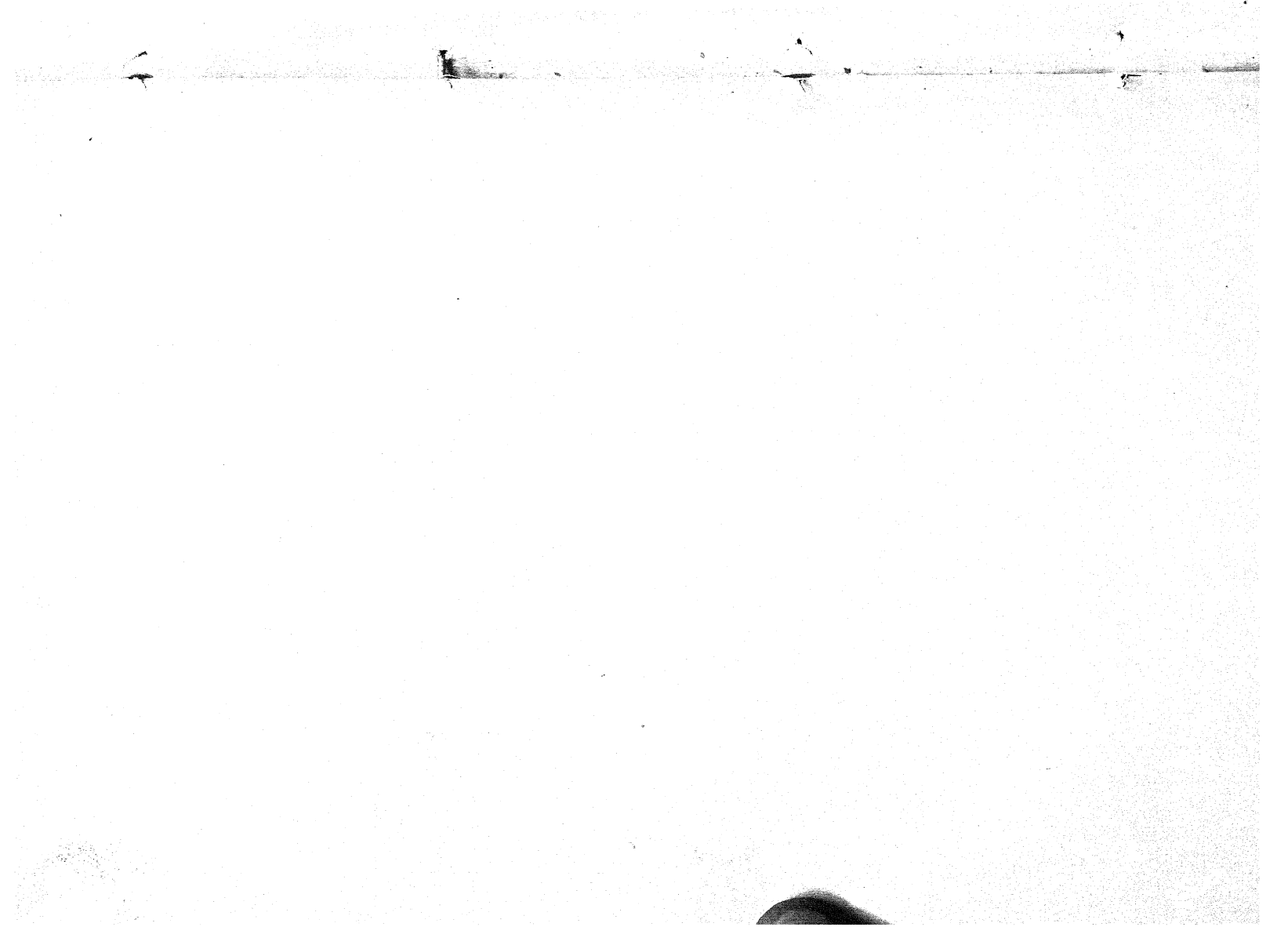
(25) WHITING, A. L., AND HECK, A. F. 1926 The assimilation of phosphorus from phytin by oats. *Soil Sci.* 22: 477–493.

FIRST INTERNATIONAL CONGRESS OF ELECTRO-RADIO-BIOLOGY

The First International Congress of Electro-Radio-Biology will be held from September 10 to 15 in the Doges Palace, Venice, according to an announcement of the International Society of Radio Biology. The object of the Congress is to study the chemical and biological phenomena of all radiations in order to coördinate the investigations of physicists, chemists, biologists, naturalists, and physicians.

The Congress will be presided over by His Excellency the Marquis Guglielmo Marconi, President of the Royal Academy of Italy, President of the National Council of Research, State Senator, and by His Excellency, Count Giuseppe Volpi di Misurata, State Minister, State Senator.

Further information may be obtained from Dr. Giocondo Protti, General Secretary of the Congress, S. Gregorio 173, Venice, Italy.



EILHARD ALFRED MITSCHERLICH

To the Sixtieth Birthday of the German Investigator

E. VON BOGUSLAWSKI[1]

Königsberg University

The name of Eilhard Alfred Mitscherlich has long been known through the literature and research institutions the world over. His methods of pot experiments and plant physiological approach to soil science have been fundamental in investigating "the law of physiological relations," on which the determination of the fertilizer requirements of the soil hinges. He is known for his methods of establishing compensating factors in field experiments and of determining heat of wetting, hygroscopicity, and climatic factors associated with evaporation, and for many other important concepts. His sixtieth birthday, on August 29, 1934, offers an occasion to sum up some of the important details of his life and work and to point out further particulars which cannot be communicated by a mere enumeration of papers.

In choosing a scientific profession, E. A. Mitscherlich followed his family's tradition. His father, Alfred Mitscherlich, was a physician and professor of the University of Berlin. His grandfather, Eilhard Mitscherlich, professor in Berlin, was the well-known chemist who contributed so much to our knowledge of organic chemistry and who devised the first polarimeter for use in sugar chemistry.

E. A. Mitscherlich studied chemistry and physics in Kiel and began his scientific work in agriculture as Rodewald's assistant. He received the degree of doctor of philosophy for his work "The evaluation of the physical properties of the soil by means of its heat of wetting." This work contains an important and original method in soil science. At the same time, by determining the soil surface, Mitscherlich introduced one of the main problems of general soil science. He was, however, chiefly interested in the physical properties of soil, in a way similar to Wollny and his co-workers and the school of Ramann. In Rodenwald's Institute he published his habilitation work "Investigations on the physical properties of soil." Even these first papers give evidence of what was to become, in course of time, one of his greatest contributions to the field of soil science: his severe and uncompromising scientific attitude. Mitscherlich, with his abundant energy, opened a fertile new field in soil science. For the younger generation, the principles of his work and his productivity both in theory and experiment are most impressive. There is scarcely a problem of general plant culture left unattacked during the first ten years of his research work.

[1] Translated from the German by S. A. Waksman.

In 1903 he published with Rodewald the method of hygroscopicity, and in the same year his first papers on the mathematical treatment of experimental results. In 1904, he constructed (independent from Livingston) his first atmometer. In the years 1907 to 1911, he did his fundamental work on the chemical methods of analysis. This was done in Königsberg, to which he had been called, as head of the Pflanzenbau Institut, in 1907. In the same year he received a call to Pasoeroean (Java), which he refused.

The outstanding difference between Mitscherlich and his colleagues in all of his activities was his original method of choosing problems in soil science. His idea was that the principal task of the science is the examination of the growth factors. This was not completely new, but it was essential for limiting the nature of the problem and the methods adopted and for the evaluation of the results.

In the first edition of his "Soil Science for Agriculturists and Foresters" (Bodenkunde für Land- und Forstwirte, 1905), in which he summarized anew his ideas of plant growth, he definitely started out on a new path distinct from geological soil science. He realized, for instance, that by extracting phosphoric acid from the soil one cannot learn about the processes that take place between the plant and the phosphoric acid in the soil. So he preferred to study the effect of the phosphoric acid in soil by means of the growing plant itself. He let the plant give the answer to the effect of phosphoric acid during the vegetation period.

He refuted Liebig's idea that the growth of plants depends mainly on the minimum factor, and conceived the crop yield as a product of the joint action of all the factors combined. For the most important hitherto known chemical and climatological growth factors he was able to confirm his inductive assumption that the crop yield approaches a maximum asymptotically with the increase of one factor. Independent of the maximum of the latter, the increase in crop yield differs only quantitatively and follows, for the same factor, the law of the constancy of the so-called "growth-factor."

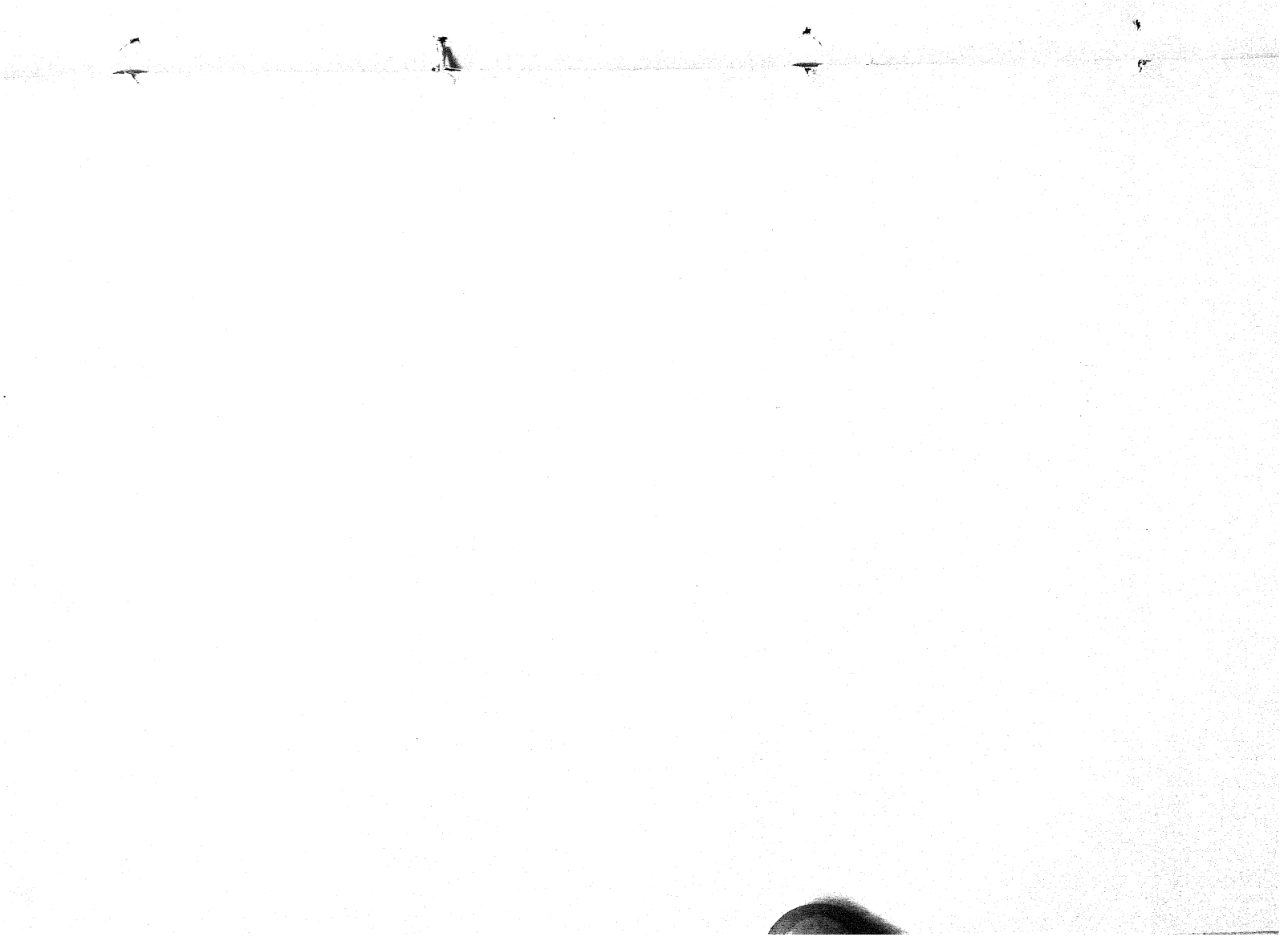
The first investigations of "The law of action of the growth factors" were carried out in Kiel. In Königsberg, he, together with his collaborators, accumulated for a period of 20 years an extensive mass of experimental data. Beginning with his scientific data, Mitscherlich utilized pot experiments for determining the fertility of the soil, so important for practical agriculture.

In 1923, the first edition of this book "The Determination of the Fertilizer Requirement of the Soil" appeared. Here, the methods of field experiments and pot experiments are compared, and the possibility is elucidated of drawing conclusions from pot experiments as applied to soil problems.

This practical utilization of his scientific results and the latter as well met with severe criticism from his colleagues, especially in his home country. A scientific fight began concerning the constancy of the "growth factor." It remained, for the time being, a fight for concepts, the exact limitation and sensitivity of all known methods not offering any counter proof.

On the basis of his own experiments, Mitscherlich can best judge for himself to what extent he has succeeded in eliminating individual factors from the factor complex. Especially recently, Mitscherlich has pointed out repeatedly that some physicochemical and chemical methods might also prove useful for the separation of the factor complexes, with special reference to the soil solution and to the surface of soil particles. He himself is now working in this direction.

Mitscherlich is highly esteemed in cultural and civil life and fulfills many honorary functions in many scientific societies. More than a hundred pupils have left his institute during the last 28 years. Four times he was Rektor of the University. Since 1922, he has been Director of the Agricultural Institute of the University. He is a co-editor (with Mez) of the *Botanisches Archiv* and of the *Biologe*, a collaborator of SOIL SCIENCE and the Russian Journal *Pedology*, and is a member of several local and foreign scientific academies. He has been for years President of the Fourth Commission of the International Society of Soil Science.



LIBRARY

ROOT HABITS OF CERTAIN CROP PLANTS AS OBSERVED IN THE HUMID SOILS OF NEW JERSEY[1]

NOLAN F. FARRIS[2]

New Jersey Agricultural Experiment Station

Received for publication August 28, 1933

During recent years considerable attention has been directed to the study of the root systems of various agricultural plants. These studies have not been prompted entirely by curiosity, even though earlier studies were begun in that manner. Later investigators have two objects in view: (*a*) to seek improvements in varieties and strains of crop plants, and (*b*) to account for the behavior of plants under different environmental conditions.

Many methods are used to improve the yield and quality of crops: Fertilizers are applied in large amounts; green manures are used to add organic matter to the soil; soil acidity is corrected by the use of lime; and the soil is kept in excellent tilth by proper and judicious cultivation. Still, in many cases, farmers are disappointed because of failure to increase yields or improve quality. The plants may be of the best approved variety, but just as a chain is as strong as its weakest link, so a plant yields in accordance with the ability of its root system to supply it with water and nutrients. It is only recently that attempts have been made to improve crops by developing varieties with superior root systems, or by so changing the soil conditions that the root systems will become more efficient. It would seem that this line of attack offers great possibilities.

Other workers have been interested in root development as a means of explaining the behavior of the same species of plants under different environmental conditions. It is evident that the differences must be manifested, either directly or indirectly, through the roots.

Heretofore, most of the root investigations have been made in the semi-arid or sub-humid sections of the western and midwestern states. These soils, which have been described by Wolfanger (43), are called "Pedocals." The fertility of these soils, in general, is high and they present no unusually difficult problems in cultivation or management.

The humid soils ("Pedalfers") of the eastern states, on the other hand, are much older soils and have been formed under different environmental condi-

[1] Part of a thesis submitted in partial fulfillment of the requirements for the degree of doctor of philosophy at Rutgers University, New Brunswick, New Jersey.

Journal Series paper of the New Jersey Agricultural Experiment Station, department of agronomy.

[2] Research assistant in agronomy.

tions. The natural fertility is usually low, and the low organic matter content influences the soil texture and structure to such an extent that, in many cases, cultivation and management are extremely difficult.

It is reasonable to expect that different soil factors have a marked influence on the root systems of plants, but very little work has been done in comparing root systems in the humid soils with those in the drier and younger soils. Hence, it has been the purpose of this study to investigate the root development of plants in relation to the factors encountered in the humid soils of New Jersey.

The literature of the subject has been extensively reviewed by Miller (24), and Weaver has compiled extensive bibliographies in his books, "Root Development of Field Crops" (41) and "Root Development of Vegetable Crops" (42). Other researches will be referred to in the discussion of observations and results in this paper.

EXPERIMENTAL METHODS

The crops chosen for investigation were corn, white potatoes, and red clover. These crops represent three distinct types of root systems. Red clover possesses a well-developed tap-root system under most conditions. Corn is recognized as a coarse feeder, and its numerous fibrous roots spread farther laterally and penetrate deeper than those of the potato. The potato plant has a more or less superficial root system.

The direct method of root examination, as developed and described by Weaver (41), was used in these investigations. This method is more desirable than the washing method used by earlier investigators.

To simplify the drawings as much as possible only the main roots and their larger branches were plotted. If the degree of branching was unusual this fact was recorded at the time of observation. In some instances only part of the root system was recorded, in order to simplify the drawings. In such cases it was assumed that the horizontal root extent was the same on all sides of the plant. The volume of soil occupied by roots was calculated on this basis. In the case of mature potato plants the entire root system was plotted, but it appears in two separate drawings. The roots extending at right angles to the row of plants are termed "lateral" and those parallel to the row are called "longitudinal."

The root systems of each crop were examined two or three times during the season, the last examination being at maturity in the case of corn and potatoes. Several plants under each treatment were examined and, as near as possible, a representative plant was chosen for root tracings.

At the time of observation samples of soil were taken near each plant studied and at different depths so as to include all soil horizons or layers in which root growth occurred. The majority of soil samples were taken at 4 and 14 inches. In a few cases samples were taken at 21 inches. These samples were air-dried for storage and later subjected to various chemical and physical tests to

determine what relations might exist between soil conditions and root growth.

At the time the soil samples were taken, volume weight samples were obtained with the Lebedev volume weight sampler (19). The moisture content and pore space of the soils were then calculated from these samples according to the method described by Lyon and Buckman (20).

The following physical and chemical tests were made on the air-dried soil samples: (*a*) the pH values, as determined by the potentiometer and quinhydrone electrode; (*b*) the organic matter content, by the Degtjareff method (13); (*c*) the readily available phosphorus, as described by Truog (38); (*d*) the rough quantitative nitrogen content, using the spot plate test devised by Morgan (25); (*e*) the available potassium, by the Bray method (3); and (*f*) the mechanical analysis, by the hydrometer method of Bouyoucos (2).

RESULTS AND OBSERVATIONS

Weather

It is well known that the weather conditions occurring immediately before and during the growing season have a marked effect on plant growth. The root systems are also affected, although in many instances the effects on this part of the plant are not so noticeable as those on the above-ground parts. However, a small change in the root system may manifest itself to a marked extent in the vegetative portions of the plant. Outside of photosynthesis and damage by wind, hail, and sun-scalding, which affect the aerial portions of the plants directly, climatic factors operate almost entirely through the root systems.

Figure 1 shows the conditions of temperature and rainfall at 5-day intervals during the months of April to September in both 1930 and 1931. These months include practically the entire growing season of each of the three crops.

The weather of 1930 was characterized by temperatures above normal and a total rainfall considerably below normal. Except for the month of June the condition was one of persistent dryness and almost continuous warmth. June was the only month with more than normal rainfall.

The year 1931 was the warmest on record (47 years) and the second driest. However, the rainfall was concentrated in the important part of the growing season from March to August, inclusive, and the distribution was, in general, more favorable. The mean temperature was above normal for every month, with July and September having the greatest departures during the growing season. Thus the season of 1931 was more favorable for crop production than was that of 1930.

Effects of soil conditions on normal root development of potatoes

The root system of the potato plant is more superficial than that of many crops such as corn, wheat, and most legumes. In Nebraska, Weaver (41) found that the roots extend horizontally to a distance of 1 to 2 feet or more and then turn more or less abruptly downward and penetrate the second or third foot of

soil. Branching is profuse throughout the root extent. The branches, however, tend to be relatively short. Weaver states that both depth of penetration and lateral spread, as well as abundance and length of branches, are greatly modified by differences in the water content and fertility of the soil.

The plants which Weaver studied were grown in a mellow loess soil and received no cultivation. The ones investigated in this study were grown on Sassafras loam and received the average cultivation. Sassafras loam is classed by Wolfanger (43) as a gray-brownerth in the Pedalfer group. It consists of a brown loam underlaid at 8 to 10 inches by yellowish brown clay loam which passes into an orange or reddish yellow friable sandy clay. Usually the lower subsoil is more sandy than the upper subsoil. The soil on which part of these tests were conducted had not been cropped for several years, and a rather heavy stand of redtop and bluegrass was turned under at the time of plowing.

The most striking feature of this study was the failure of the potato plants

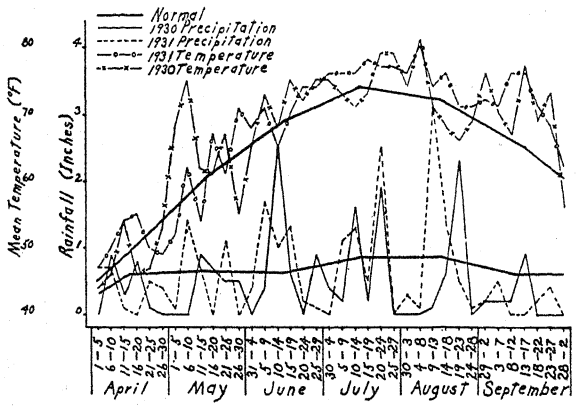


FIG. 1. RAINFALL AND MEAN TEMPERATURES BY 5-DAY PERIODS DURING THE GROWING SEASON IN 1930 AND 1931

to develop extensive root systems. In only a few of the plants examined did the roots penetrate lower than 10 inches.

The root systems of the potato plants had apparently almost reached their maximum development at 70 days after planting. Reference to the illustrations will show that the root systems of the mature plants (110 days old) are only slightly larger than those of the 70-day-old plants.

There was some evidence of root pruning from cultivation but the plants seemed to be able to regenerate these roots at a sufficiently rapid rate to insure vigorous development. Examination of the longitudinal roots, which were not injured by cultivation, shows that there is very little difference between the root systems of the 70-day-old plants and the mature plants. There is no evidence in these studies, however, to show whether different methods of cultivation would improve the plants through increased root development. Such studies have been made but they were carried out on different soils.

In general, then, the average root systems of potatoes studied in this problem were markedly reduced as compared with those reported by previous investigators. The reasons for these differences must therefore be sought by examinations of the climatic and soil conditions under which the studies were conducted.

The potato plant requires a relatively large amount of water for the best development. The best root development is obtained when the plant receives small applications of water just often enough to maintain continuous growth. Thus, it is found that the greatest yields of potatoes have been obtained under irrigation. This may be explained by the fact that the root systems are stimulated to the highest degree and a greater and more efficient absorbing root surface is obtained, thus furnishing the plants with large amounts of water and mineral nutrients.

In humid climates rainfall is relied upon to furnish water to plants. In many cases the annual rainfall is high but most of the precipitation is concentrated at different periods during the year and may not be available when most needed by the crop.

During 1930 the precipitation at New Brunswick was below normal for all months except June. However, the rainfall was rather well distributed throughout the growing season, as shown in figure 1. Therefore, satisfactory yields were obtained in most cases. The rainfall for the growing season of 1931 was only slightly greater.

In the majority of the plots, at the times of observation, the moisture in the surface soil was equal to, or greater than, that of the subsoil. The same condition existed throughout the growing season so far as is known. The rainfall was light and well distributed, and the supposition is that the moisture did not penetrate far into the subsoils except in a few locations. Weaver (41) found that in sub-humid soils root development was stimulated in regions where moisture was concentrated. This may or may not be the case in humid soils. The fact that the surface soil contained as much moisture as the subsoil may be one reason for the failure of the roots to penetrate to deeper horizons. However, it does not explain the reason for limited horizontal root growth in the surface soil. Other factors must be studied in order to explain this.

The pH values of the soils, in general, ranged between 4.5 and 6.0. In practically every case the pH of the subsoil was slightly higher than that of the surface soil. Previous workers have reported that soil acidity increases markedly during the growing season. The tables show that the pH values for the subsoil of the different plots were quite uniform and remained so throughout the season. The surface soil, however, varied considerably, and the values obtained when the plants were mature are slightly higher than those obtained when the plants were young. There are two explanations for this behavior: first, it may be caused by the plants directly, as some investigators propose; second, an increase in acidity may result from the turning under of organic matter, and as this organic matter decomposes the acidity decreases (17). This explanation is borne out in these studies by the fact that the sub-

soil changed very little in pH, while the surface soil, which contained the organic matter, is markedly affected. Also the acidity was less for the second year of testing, and the soil "humus" was greater. Probably both explanations apply to a greater or less extent. At 70 days after planting, when the plants were growing vigorously, the pH of the surface soil was lower than when the plants were mature. This was the case in both 1930 and 1931.

Table 1 shows the average pH and the average soil organic matter of all plots for the four series of observations in the size of seed piece and spacing experiment.

The pH values found are not so low as to interfere with the development of the potato plant. This crop is very tolerant of acid conditions, and this fact is utilized in the control of potato scab (*Actinomyces scabies*).

The organic matter of the soil on the experimental plots was very low, as is characteristic of the soils of this region. There were no significant differences between the various plots. In 1930 the organic matter plowed under did not

TABLE 1

Average soil acidity and percentage of organic matter of potato plots, 1930 and 1931

	1930		1931	
	6/20	7/22	6/25	7/3
Surface soil:				
pH	4.9	5.1	5.0	5.1
Organic matter, *per cent*	1.4	1.3	2.1	2.3
Subsoil:				
pH	5.5	5.6	5.2	5.2
Organic matter, *per cent*	0.5	0.4	1.0	0.9

decompose readily, because of dry weather, so that the percentage of organic matter (humus) was only about half that found in 1931 when more complete decomposition had taken place. The values for the subsoil were about one-third to one-half of those for the surface soil. Organic matter is important in improving the water-holding capacity of the soil, and this may account, in part, for the surface soil having a high moisture content at the time of sampling.

The texture and pore space of the soil are important factors in the development of root systems. Fine-textured soils have greater pore space, but in humid soils more of this pore space will be occupied by water than will that of a coarser textured soil. This factor is important in regions where the rainfall is heavy and soils tend to waterlog. Reduced aeration, in such cases, results in poor plant development. Therefore, it is the custom to improve the aeration of fine-grained soils by increasing the organic matter content.

In these studies most of the soils were either sandy loams or clay loams. The subsoils were generally heavier and in many instances were classed as clays. On drying, these soils tended to become very hard, especially just below

the surface. In several instances the soil was so hard as to prevent the taking of volume weight samples with the sampling tube. It is reasonable, therefore, to suppose that roots would have to overcome considerable resistance in penetrating lower horizons, and since the root system of the potato plant tends to be more or less superficial this resistance might well be sufficient to prevent deep penetration. However, no great penetration was observed even in soils which tended to be sandy.

The pore space of the soils utilized in these studies, in general, varied from 40 to 50 per cent. The pore space of the subsoils was considerably lower. These values are sufficiently high to make aeration a problem in years of high precipitation.

Effects of different fertilizer ratios on potato root development

In 1930 the mature root systems of Irish Cobbler potatoes were investigated in a fertilizer ratio test reported by Martin, Brown, and Sprague (22). Investigations were made on plots receiving the following fertilizer ratios: 0–0–15, 0–15–0, 0–6–9, 9–0–6, 9–6–0, 6–3–6, and 15–0–0.

The general effect of phosphate fertilizers on soils deficient in available phosphorus has been to cause deeper rooting, and, in regions where droughts occur, phosphates are applied to induce shallow-rooted plants to send their roots down to the moist subsoil.

With regard to nitrates the evidence is not quite so clear. Weaver (41) states that where roots come in contact with a soil layer rich in nitrates, they not only develop much more abundantly and branch more profusely but fail to penetrate as far into the deeper soil. On the other hand, Turner (39) claims that nitrates increase the growth of the tops, which in turn require more of the manufactured carbohydrates, thus reducing the carbohydrate supply of the roots and causing less root development. However, it would seem that increased top growth would at the same time provide for an increase in the manufactured plant food. In such case, the roots would not be deprived but would develop more abundantly.

In the fertilizer ratio test investigated in this study, there was apparently little correlation between the fertilizer ratio and the yields and root development.

Table 2 gives the number of main roots per plant, the soil volume occupied by roots, and the yields for the various fertilizer ratios studied. The yields for 1930 were discarded because of heavy infection of spindle tuber in all plots. However, the individual plants studied were apparently normal. The yields given here are the averages for the years 1925–1928. These yields can not be too greatly relied upon since they were observed in other years than those of the root examinations, but they are given in an attempt to explain the results.

The highest yields obtained were from the plots on which the fertilizer ratio 6–3–6 was used. The plants of this treatment had a relatively high number of roots but the soil volume occupied was very low. The lowest yields were

obtained on plots which received the fertilizer ratio 15–0–0. This ratio also gave plants with a low number of roots but the volume occupied was high, thus showing that high concentration of nitrates does not necessarily limit root development. But the supposition is that when a great amount of root and top growth occurs the tubers are not formed and developed as extensively as with other ratios.

According to these data a great number of roots does not necessarily mean a high yield, as shown in the ratio 0–6–9. The high phosphate ratio, 0–15–0, seemed to cause an increase in root development, both in number of roots and branches and extent, but here again the yield was low. The root systems of some of these plots are shown in figure 2.

The conclusions that can be drawn from these data are that extensive root development is not necessarily correlated with high yield and that a fertilizer ratio having medium to large amounts of nitrogen and potassium and a small amount of phosphates gives the highest yields on this soil. The whole problem

TABLE 2

Relation of fertilizer ratio to yield, number of main roots, and volume of soil occupied by roots of potato plants, 1930

FERTILIZER RATIO	NUMBER OF MAIN ROOTS PER PLANT	SOIL OCCUPIED BY ROOTS	YIELD PER A., 1925–1928
		cu. in.	*bu.*
0–15– 0	38	2,660	265
0– 6– 9	50	2,016	255
9– 6– 0	35	2,160	295
6– 3– 6	44	1,260	320
0– 0–15	26	1,200	290
9– 0– 6	36	3,280	315
15– 0– 0	31	3,600	240

needs further investigation before accurate deductions can be made. It is quite probable that the spindle tuber disease affected the root development considerably even though the plants examined appeared to be normal. It is also possible that the fertilizer ratios might markedly affect synthesis and storage of carbohydrates in the tubers without greatly affecting the root system, provided the root system is adequate in all cases.

Effects of size and spacing of seed pieces on potato root development

This experiment was a study of the effects of size and spacing of seed pieces on the yield of Irish Cobbler potatoes and was similar to the one reported by Sprague and Evaul (32). Seed pieces weighing ½ ounce, 1 ounce, and 1½ ounces were spaced at various intervals, and observations of the root systems were made on the various spacings of each of the three sizes of seed pieces. This experiment was conducted in both 1930 and 1931.

During recent years the potato grower of New Jersey has found it to his

advantage to use the smallest sized seed pieces and the widest spacings which will insure optimum development and yield. The most profitable combination is that which will make the most efficient use of the soil and climate at hand. Seed pieces must be large enough to give the plants a good start and the plants should be so spaced that all parts of the soil horizons in which the roots grow will contribute moisture and nutrients to the growing plants.

In brief, the results obtained by Sprague and Evaul (32) were as follows: (*a*) Reducing the space between the seed pieces of the same size increased

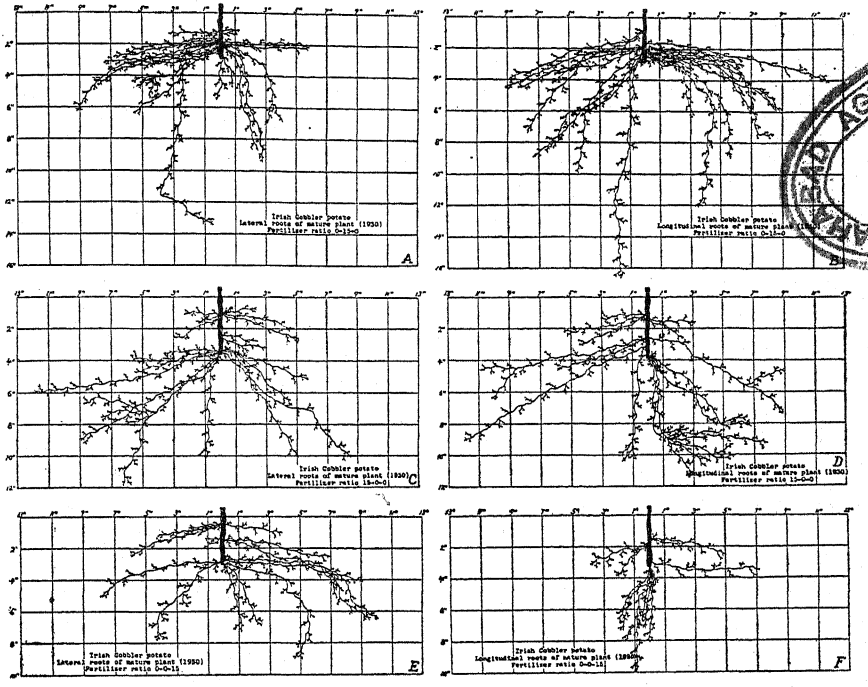


FIG. 2. ONE-HALF OF THE ROOT SYSTEMS OF MATURE IRISH COBBLER POTATO PLANTS OBSERVED IN THE FERTILIZER RATIO TEST, 1930

(A) Lateral roots. (B) Longitudinal roots. Fertilizer ratio 0–15–0.
(C) Lateral roots. (D) Longitudinal roots. Fertilizer ratio 15–0–0.
(E) Lateral roots. (F) Longitudinal roots. Fertilizer ratio 0–0–15.

yields; (*b*) increasing the size of the seed piece greatly increased yields when the spacing in the row remained the same; (*c*) when the total weight of seed used per acre remained constant, the highest yields were obtained from the $\frac{1}{2}$-ounce seed pieces and the lowest from the $1\frac{1}{2}$-ounce pieces; (*d*) when the amount of seed used per acre was subtracted from total yields, the net yields increased with the rate of planting for each size of seed piece; and (*e*) the greatest returns of crop per bushel of seed were obtained from $\frac{1}{2}$-ounce seed pieces spaced at 12 inches in the row.

At the time these tests were carried out it was not clear why the foregoing results were obtained, since no examinations of the root systems were made. Two explanations were offered: (*a*) Closer spacing caused the roots to penetrate deeper into the subsoil, and since a greater soil volume would be occupied the moisture supply of the plant would be greater during the critical periods in July and August; and (*b*) closer spacing may result in a more complete utilization of the fertilizer added.

In these studies the root systems of plants of each treatment were examined 70 days after planting and at maturity. In general, the same relationships existed among yields as those noted in the earlier tests. The yields in 1931 were all lower than expected, however. This was presumably due to the high amount of precipitation in the early part of May, causing an excessive growth

TABLE 3

Effects of size of seed pieces and spacing on the yields of potatoes, 1930–1931

SIZE OF PIECE	SPACING	SEED USED PER ACRE	TOTAL YIELD PER ACRE	YIELD PER BUSHEL OF SEED
oz.	*in.*	*bu.*	*bu.*	*bu.*
½	12	9.1	124	13.6
½	9	12.1	143	11.8
½	7½	14.5	156	10.8
½	6	18.2	171	9.4
1	18	12.1	162	13.4
1	15	14.5	158	10.9
1	12	18.2	185	10.2
1	9	24.2	190	7.9
1½	22½	14.5	139	9.6
1½	18	18.2	154	8.5
1½	13½	24.2	173	7.1
1½	9	36.3	187	5.2

of vines and checking the formation of tubers. Table 3 summarizes the results indicated in the foregoing for the two years 1930 and 1931.

The results agree, for the most part, with those reported by Sprague and Evaul. An examination of the root systems should yield information as to the causes for such results.

Figure 3 represents one-half of the total root system of plants from the various sized seed pieces spaced at 9 inches in the row. The examinations were made 70 days after planting. The most striking fact is the apparent extent of the root systems from different sized seed pieces. The ½-ounce seed pieces show root systems consistently smaller than the larger seed pieces, regardless of the spacing in the row. On the other hand, the root systems of the 1½-ounce seed pieces were consistently larger. The spacing of the plants in the row apparently had little effect on the root systems at this stage. At the

spacing of 9 inches, plants from the ½-, 1-, and 1½-ounce seed pieces had root systems occupying 128, 720, and 2,048 cubic inches respectively. Even if the

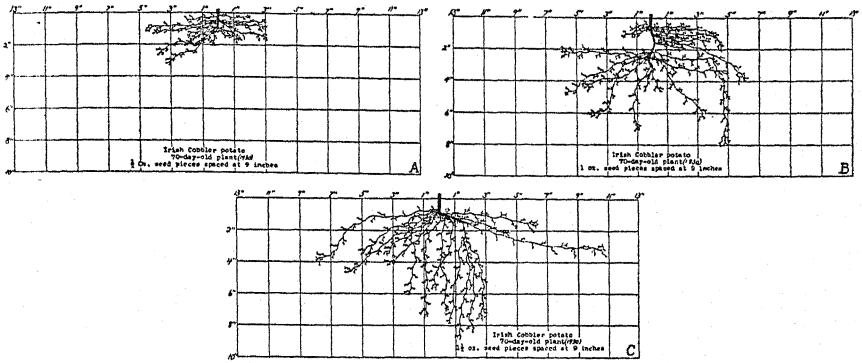


FIG. 3. ONE-HALF OF THE ROOT SYSTEMS OF 70-DAY-OLD IRISH COBBLER POTATO PLANTS GROWN FROM VARIOUS SIZED SEED PIECES AND SPACED AT 9 INCHES IN THE ROW, 1930
(A) ½-oz. seed piece. (B) 1-oz. seed piece. (C) 1½-oz. seed piece.

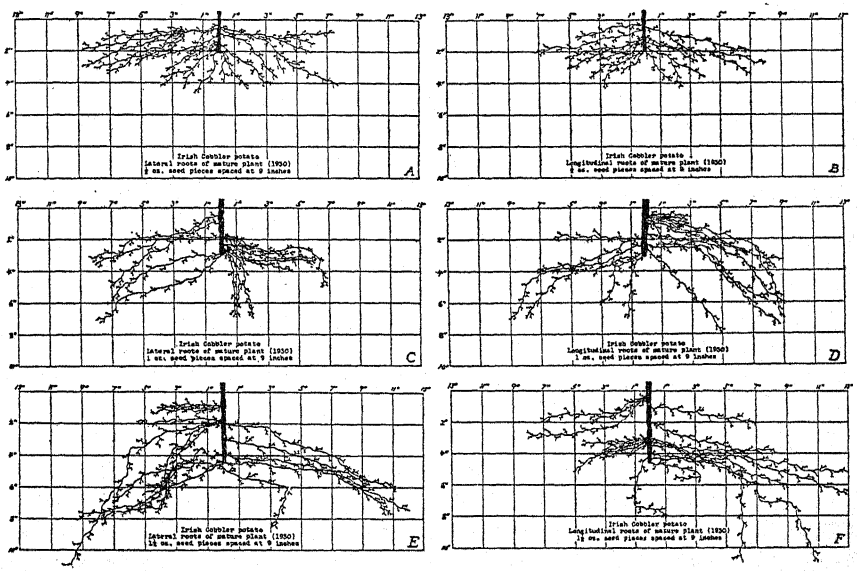


FIG. 4. ROOT SYSTEMS OF MATURE IRISH COBBLER POTATO PLANTS GROWN FROM VARIOUS SIZED SEED PIECES AND SPACED AT 9 INCHES IN THE ROW, 1930
(A) Lateral roots. (B) Longitudinal roots. ½-oz. seed piece.
(C) Lateral roots. (D) Longitudinal roots. 1-oz. seed piece.
(E) Lateral roots. (F) Longitudinal roots. 1½-oz. seed piece.

plants had produced extensive root systems they would hardly have been large enough at this age to make competition a factor.

At maturity the general character of the root systems was about the same. These are shown in figure 4. On the whole, the lateral roots appear to be less extensive than the longitudinal roots, indicating that root pruning during cultivation may be a factor.

In 1930 there was a progressive increase in yield from the ½-ounce to the 1½-ounce seed pieces spaced at 9 inches. In 1931 the yield for the 1½-ounce pieces was slightly less than that for the 1-ounce pieces but this can easily be due to chance variation. The results indicated by Sprague and Evaul correspond with the former condition. The figures given in table 4 are averages for 1930 and 1931, and show that an increase in yield is accompanied by a corresponding

TABLE 4

Effects of size of seed pieces spaced at 9 inches on the yield of potatoes and the soil volume occupied, 1930–1931

SIZE OF SEED PIECE	YIELD PER A.	VOLUME OF SOIL OCCUPIED BY ROOTS OF A SINGLE PLANT
oz.	*bu.*	*cu. ft.*
½	143	25.2
1	190	61.6
1½	187	75.5

TABLE 5

Effects of size of seed piece on yield of potatoes and soil volume occupied when the same amount of seed per acre is used, 1930–1931

SIZE OF SEED PIECE	SPACING IN ROW	SEED PER A.	YIELD PER A.	VOLUME OF SOIL OCCUPIED BY ROOTS IN AN EQUAL AREA
oz.	*in.*	*bu.*	*bu.*	*cu. ft.*
½	7½	14.5	156	107.7
1	15	14.5	158	129.8
1½	22½	14.5	139	77.3
½	6	18.2	166	116.1
1	12	18.2	185	120.9
1½	18	18.2	154	49.5

increase in root volume, if the 3-bushel difference between the 1- and 1½-ounce seed pieces is disregarded.

If the plots in which the same amount of seed per acre is used are compared, the figures shown in table 5 are obtained.

The root volume of a single plant was multiplied by 3 in the case of the ½-ounce seed piece and by 2 in the case of the 1-ounce seed piece in order to bring the number of plants per unit area to a common basis.

The figures show that the yield from the 1-ounce pieces is greater than that from the ½-ounce pieces and also that the root volume increases. Furthermore, the yield from the 1½-ounce pieces is below that from the ½-ounce pieces, and

the same is true of the soil volume occupied. Hence, it may be concluded that the plants produced by 1-ounce seed pieces utilize the soil more efficiently than do those produced by the ½-ounce or 1½-ounce pieces. Table 3 shows that the greatest yield per bushel of seed used is produced by the ½-ounce seed pieces spaced at 12 inches. This also must be due to the more efficient use of the fertilizer and soil moisture.

It is a common practice in this region to apply large amounts of fertilizers to a potato crop. This has given good results as far as the potatoes are concerned, but there is a certainty that all the fertilizer is not utilized by the plants. Several investigators have reported that the residual effects on the following crops are quite marked. This indicates that less fertilizer is required as the plants are spaced farther apart in the row.

AGRICULTURE LIBRARY

The evidence in these studies seems to show that the large amounts of fertilizers applied to the surface soil, where moisture is usually plentiful, tend to produce limited root systems both in the horizontal and the vertical directions. There is need for information on the effects of fertilizers applied to the lower soil horizons. As long as soil moisture is sufficient in the surface soil an extensive root system is not required where large amounts of fertilizers are used, but in times of drought a plant with a deep-seated root system has a decided advantage over one with a superficial system. It may be that in these soils deeper applications of fertilizers would result in deeper root systems.

Effects of soil conditions on root development of red clover

The clover plants utilized in these studies were a part of a strain test of red clover. The results of a previous test of this nature are given by Sprague, Evaul, Reuszer, and Farris (33). Strains from Ohio, Michigan, and France were studied, both spring and fall seedings being used.

Most investigators have reported that red clover possesses a tap root which penetrates very deeply. Also an extensive system of laterals is usually present. The deeply penetrating character is associated with a deep, mellow soil which is well drained. The roots do not penetrate far into heavy, wet soil. The early work of Hays (24) in Minnesota showed that red clover, in addition to being deeply penetrating, also possessed a great number of laterals, in many cases penetrating as far as, or farther than, the tap root itself.

Weaver (41) found that root development in the second year of growth consisted mainly in deeper penetration and growth of a few additional laterals. In other words, the territory later to be fully occupied by the roots is blocked out early in their growth.

In New York (24), on a heavy clay soil, the tap roots of red clover reached a depth of 34 inches the first season, and branches occurred throughout their length, with some of the branches extending 12 inches from the tap root.

In the present study the root systems of the clover plants observed tended to be shallower than would be expected from previous reports on the root development of this plant. In general, growth during the first year was limited to

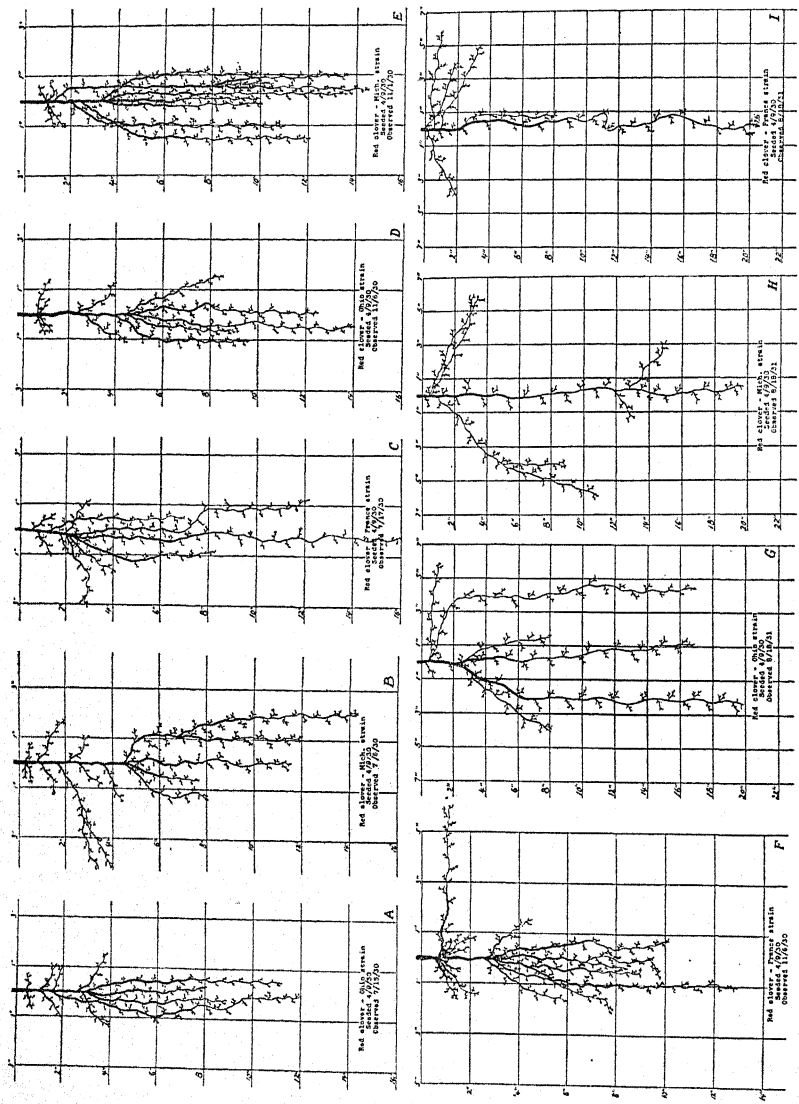


FIG. 5. ONE-HALF OF THE ROOT SYSTEMS OF DIFFERENT STRAINS OF RED CLOVER SEEDED APRIL 9, 1930

(A) Ohio; 3 months old. (B) Michigan; 3 months old. (C) France; 3 months old.
(D) Ohio; 7 months old. (E) Michigan; 7 months old. (F) France; 7 months old.
(G) Ohio; 16 months old. (H) Michigan; 16 months old. (I) France; 16 months old.

about 3 inches in the horizontal direction and 14 inches in depth. This is a decided contrast to the observations of Weaver in Nebraska, where he found roots of 1-year-old plants penetrating to a depth of 4 and 5 feet and branches extending to 8 or 12 inches in the horizontal direction before turning downward. Evidence from these studies seems to indicate that the amount of soil moisture at the time of seeding is an important factor in the later development of the root system.

Figures 5 and 6 represent one-half of the root systems of the plants studied during 1930 and 1931.

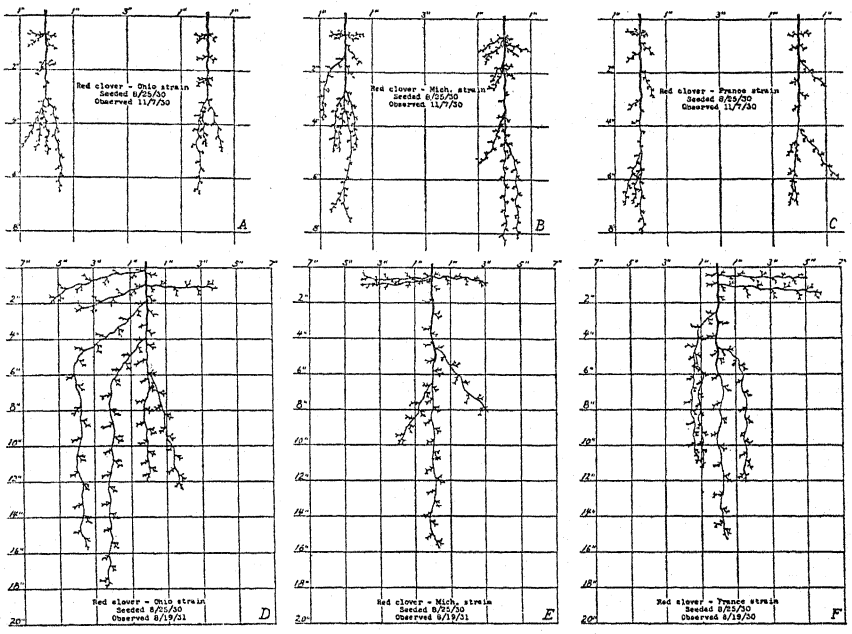


FIG. 6. ONE-HALF OF THE ROOT SYSTEMS OF VARIOUS STRAINS OF RED CLOVER SEEDED AUGUST 25, 1930

(A) Ohio; 2½ months old. (B) Michigan; 2½ months old. (C) France; 2½ months old.
(D) Ohio; 12 months old. (E) Michigan; 12 months old. (F) France; 12 months old.

At the time of the spring seeding, April 9, 1930, the soil was very dry, and little precipitation occurred until the middle of June, as is shown in figure 1. This slowed up germination of the seed and undoubtedly had a marked effect upon the formation of the root systems.

The first observations were made about June 13, 1930, when the plants were about 35 days old. Since about an inch of rain fell just prior to this examination, the soil was in good condition as regards moisture. The moisture content of the soil at this time was about 20 per cent and that of the subsoil about 22 per cent. It was evident that the branching was much more extensive than is

usual with plants of this age. The French strain was especially greatly branched. The depth of penetration was only about 7 inches.

At the second observation, July 15, 1930, the moisture content of the soil was only about half that at the previous examination. The root systems shown in figure 5 still indicate a noticeable modification of the tap root system. It was difficult, in most cases, to determine which was the tap root below a depth of 4 inches. The roots had extended to a depth of 12 to 14 inches at this time, and the branches extended laterally about 2 inches.

The last observation of the spring seeding in 1930 was made about November 5, the plants being about 7 months old at this time. The moisture of the surface soil was about 15 per cent and that of the subsoil was about 9 per cent. The roots had penetrated but little farther than they had at the previous examination (fig. 5). The plants of the French strain were, on the whole, more shallow rooted than the native strains, and branching was more extensive.

Three observations of the spring seeding were made during 1931. The moisture supply was ample and well distributed throughout the growing season. The roots had apparently made little growth during the winter months, as the distribution was about the same May 15, 1931 as it was the previous fall. However, rather rapid development occurred throughout the growing season of 1931. In July the roots had penetrated to about 17 inches and the lateral branches extended to over 5 inches. At the time of the last observation, August 18, 1931, the root systems were about as pictured in figure 5. In most cases, however, the French strain still showed greater branching and a more superficial root system.

The root systems of the plants seeded in the fall presented entirely different characteristics. The seeding was made August 25, 1930, at a time when the moisture content of the soil was very high. The observations made on November 7, 1930, when the plants were about 75 days old, showed that the root systems were more distinctly of the tap root type than was the case with the spring seeding. Little difference between the strains was noted at this time. Figure 6 illustrates the root systems at this observation.

More extensive root growth took place during the winter months than was the case with the plants of the spring seeding. The depth of penetration increased about 3 inches and the lateral spread about 2 inches. It is possible that the plants grew more vigorously in the early spring than did those of the spring seeding.

In July the tap roots had penetrated to a depth of about 14 inches and the lateral branches had reached about 4 inches.

By the latter part of August the tap roots had reached about 16 inches in depth, which is a greater depth than for the spring seeding plants of the same age. Here again, the strain from France had a more branched and superficial root system.

The pH of the soil was fairly uniform throughout the experiment. The average pH of the surface soil was 6.1 during the first year and decreased to 5.9

for the second year. The acidity of the subsoil was practically constant. The lower value for 1931 is undoubtedly due to the utilization of lime by the plants. Since the red clover plant is very intolerant of acid conditions it is possible that better growth would have occurred if the soil acidity had been less.

The organic matter content of the soil was slightly higher the second year, especially in the surface soil, the values for 1930 being 1.6 per cent for the surface soil and 0.9 per cent for the subsoil. In 1931 the organic matter content of the surface soil was 2.1 per cent and that of the subsoil 1.2 per cent. The amount of organic matter was so uniform throughout the plots that any differences occurring between the various strains can not be attributed to this soil factor.

The determinations for phosphorus, nitrogen, and potassium indicate that by far the greatest amounts of available nutrients, especially phosphorus, are concentrated in the plow zone. Evidently there is little loss of nutrients by leaching in this soil.

The soil which was utilized for these plots is a little heavier than that on which the potatoes were grown. Most of the surface soil is classed as a clay loam while the subsoil is a sandy clay or clay. The pore space of the surface soil averaged about 48 per cent and that of the subsoil a little lower. The subsoil is very heavy and hard when dry, and roots would have to overcome considerable resistance in penetrating it in that condition.

The number of branch roots did not appear to increase during the second year of growth. The volumes of soil occupied by roots are much greater the second year, largely because of the deeper penetration of the tap roots and their branches.

An additional observation was made of native red clover in the fall of 1931 and the spring of 1932. The clover was seeded in the spring of 1931 on a light sandy loam soil underlaid by light sandy loam subsoil. In November the plants had well-developed tap roots penetrating to depth of about 30 inches. The laterals had reached a distance of about 5 inches from the tap root. In April 1932, the tap roots had reached a depth of about 36 inches. Evidently the favorable moisture conditions and light soil had materially aided the development of a good tap root system on this field.

Effects of soil conditions on the root development of corn

The corn plant has a coarse fibrous root system which spreads widely and penetrates deeply, according to several investigators. Most observations have been made on deep, mellow, fertile soil where one would naturally expect root systems to attain a maximum development. Like the other cereals the first whorl of roots arises within an inch or two of the surface of the soil, even if the seed is planted several inches deep. All the roots arise from the nodes of the stem in whorls and it is not uncommon to find roots arising from the first

one or two nodes above the surface of the soil. However, these roots do not branch until they reach the soil.

In these studies the root systems of several corn varieties were examined on different soil types in both 1930 and 1931. These observations included both checked and drilled corn. In 1931, root examinations were made in a test of different methods of corn cultivation.

Weaver (41) made observations of corn grown on loess soil in eastern Nebraska when the plants were 36 days old. At this time the roots extended laterally to 2.5 feet and were confined largely to the first foot of soil. In the present studies 44-day-old corn plants of the Mercer White Cap variety, grown on a fairly light sandy loam soil, were examined June 26, 1930. These plants were spaced 40 inches apart each way. Figure 7 (A) represents the

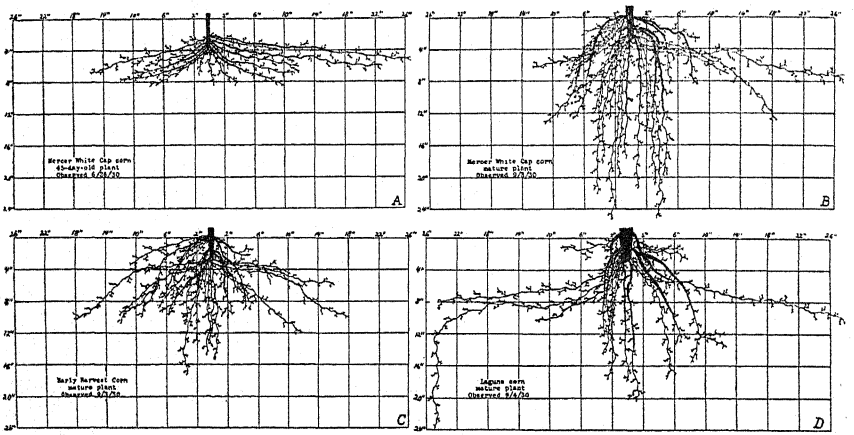


FIG. 7. ONE-HALF OF THE ROOT SYSTEMS OF THREE VARIETIES OF CORN, 1930
(A) Mercer White Cap; 45-day-old plant. (B) Mercer White Cap; mature plant.
(C) Early Harvest; mature plant. (D) Laguna; mature plant.

appearance of the plant roots at this time. Most of the roots extended laterally to 16 or 18 inches and very few had penetrated beyond a depth of 8 inches.

A mature root system of a plant grown on the same soil is shown in figure 7 (B). The most striking fact is the short extension of the lateral roots. There was evidence of considerable root pruning from cultivation, which accounts for this appearance. The depth of penetration seemed to be about 24 inches. Many of the brace roots formed at or above the soil surface were among the most deeply penetrating ones.

The soil moisture content was low at the time of observation, September 3, 1930, but figure 1 shows that the moisture was distributed throughout the growing season so that, in all probability, normal growth took place.

The root systems shown in figure 7 (C and D) are those of two different varieties of corn. C is a variety known as Early Harvest, which has been

developed by D. H. Rising of Easton, Pa. This variety should be well adapted to this region. The root system of this variety was much less extensive than that of the Mercer White Cap. The maximum spread was 18 inches, and the greatest depth was about 16 inches. D is the Laguna variety. The seed of this variety came from Mississippi. The top growth was exceedingly tall and rank. The roots showed evidence of extensive pruning in the upper few inches of soil but several roots extended horizontally as far as 28 inches and vertically to a depth of 24 inches.

These studies indicate that various varieties of corn may differ widely in their root systems. It is also entirely possible that even different plants of the

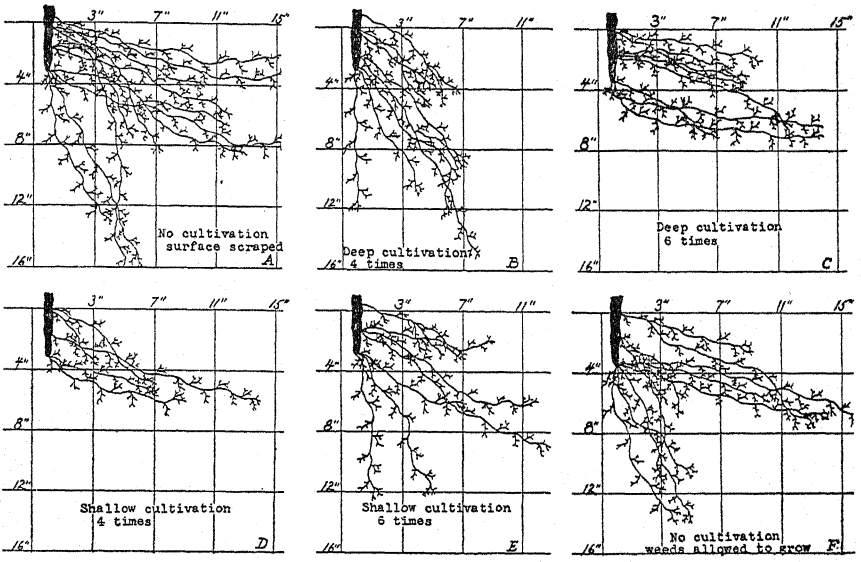


FIG. 8. ONE-FOURTH OF THE MATURE ROOT SYSTEMS OF LANCASTER SURE CROP CORN UNDER DIFFERENT METHODS OF CULTIVATION, 1931

(A) No cultivation, surface scraped. (B) Deep cultivation four times.
(C) Deep cultivation six times. (D) Shallow cultivation four times.
(E) Shallow cultivation six times. (F) No cultivation, weeds let grow.

same variety will show great differences in their root systems, since corn varieties are not homozygous. It would be interesting to study the root systems of selfed lines of corn in addition to single and double crosses between the lines.

In 1931 a cultivation experiment was conducted with Lancaster Sure Crop corn. The soil utilized for this experiment had had 3 or 4 inches of the surface soil removed several years previously and it had been seeded to timothy for 3 or 4 years previous to this experiment, so that a fairly heavy sod was plowed under. The surface soil was classed as a clay or clay loam and the subsoil as a sandy loam. The plants were spaced at 40 inches each way and the plots cultivated in both directions.

Figure 8 illustrates the root systems found in these observations.

The highest yields were obtained from the plots receiving deep cultivation six times and the next highest from plots which were cultivated shallow six times. However, these yields were only slightly greater than the ones obtained from the plots which received no cultivation, the weeds being kept down by scraping with a hoe. Shallow cultivation and deep cultivation four times were apparently not as effective as the greater number of cultivations. The yields of the plots in which the weeds were allowed to grow were, of course, decidedly inferior.

An examination of the root systems showed that in the plots receiving no cultivation, the weeds being kept down by hoeing, the root systems were much more extensive than in the cultivated plots. The volume occupied by the root system is 9,464 cubic inches, while that of the plots giving the highest yields is only 3,388 cubic inches. The plots in which the weeds were allowed to grow had very extensive root systems, but apparently the weeds left little moisture and nutrients for the corn plants.

Other investigators have reported that shallow cultivation or none at all gives better results than deep cultivation (12). The differences are so slight in this experiment that definite conclusions can not be drawn without further evidence. A suggestion may be proposed, however, that where large amounts of fertilizer are used and rainfall is abundant the root systems, even though not extensive, are able to supply the plant with adequate moisture and nutrients. Furthermore, on heavy soil, root pruning by deep cultivation may be offset by loosening and aerating the soil. The plants may be able to regenerate roots at a sufficiently rapid rate to insure good development of the plant. This problem requires more investigation on different types of humid soils. It is reasonable to suppose that humid soils require different cultivation, as well as other treatments, from the soils in the sub-humid or semi-arid regions.

The other soil factors and plant responses were about the same as those discussed for potatoes and clover in the previous sections.

GENERAL DISCUSSION

One conclusion that can be drawn from these studies is that the root systems of many crop plants are decidedly different on the humid soils of New Jersey from those reported by workers in other regions. The general forms of the root systems may be similar but they are much less extensive than those observed in the lighter and drier soils of the western and mid-western states. Weaver reports observations of potatoes in which the roots extended laterally more than 2 feet and penetrated to a depth of more than 4 feet. In this study very few roots extended laterally more than 1 foot and the vertical depth to which they penetrated was seldom more than 10 to 12 inches. Reports have been made of mature red clover in which the tap roots penetrated to depths of more than 8 and 10 feet, but observations in this locality failed to discover roots which penetrated farther than 3 feet, and lateral branching was also noticeably limited. Other workers have observed corn roots which had a lateral spread of

over 4 feet and a vertical extent of 8 feet and more, whereas the corn roots in this soil were limited to the first 2 feet of soil and extended laterally not more than 2 feet.

In general, the number of roots per plant and the amount of branching of the main roots, in each crop studied, seemed to be less than those observed by other investigators in other soil groups.

The different soil factors must be held accountable for these differences, since the roots are very little affected by conditions above their immediate environment. It is usually the roots which influence the above-ground parts of the plants.

The soil reaction is ordinarily corrected by liming to suit the requirements of a particular crop, and this factor does not seem to be very influential in modifying the root system as long as the plant as a whole makes the optimum development.

The main influence of soil organic matter on fertilized soils is to increase the water-holding capacity of the soil and to improve the structure of heavy, fine-textured soils. In the soils on which these tests were conducted very little organic matter was found below the plow zone. Even in soils where roots penetrate to great depths, little organic matter is present in the lower horizons. Apparently then, this factor influences root development very little on these soils. If it were very influential the lateral spread of roots in the surface soil should be greater than has been observed.

The pore space found in these soils is estimated to be adequate except during a period when high precipitation occurs. Some soils of this region are not well drained, and pore space may then be a factor influencing normal root development.

The soil texture itself should not be a very important factor in root development as long as moisture and nutrients are adequate. Roots have been found to penetrate deeply into heavy clay subsoils and even through hardpans, but this probably occurs when these layers are moist and soft.

It is believed that the factors which most influence root development in the humid soils are moisture and mineral nutrients. Since the rainfall is usually ample in this region, the surface soil contains a fair amount of moisture at all times. Even after several days of dry weather the surface soil may contain as much moisture as the subsoil. Thus the necessary stimulus is not provided to cause plants to penetrate deeply into the soil for moisture. In the case of clover it is suggested that the moisture content of the soil at the time of germination and early seedling growth has a great influence on the formation of the root system. Plants which start in a relatively dry soil seem to have shallower and more branched root systems, even at maturity, than those plants which start their growth with an adequate supply of soil water.

Coupled with the moisture supply is the supply of available nutrients. Large amounts of commercial fertilizers are used on the soils of this region and from determinations made in this study most of the available nutrients are

concentrated in the surface soil or plow zone. Apparently very little is carried down into the lower horizons. Thus it seems natural to assume that the growth of plant roots would be restricted by chemotropism to those soil layers in which the most available nutrients occur. Also where very large amounts of fertilizer are used, as with potatoes, the root growth would likewise be restricted in a horizontal direction. Hence, plants can be spaced closer together in order to utilize more of the soil, or the fertilizer rate can be reduced for the wider spacings.

Several additional problems have presented themselves during these investigations. In the first place no studies were made of the influences of soil organisms on root growth. It is almost certain that the action of micro-organisms may have considerable influence on root development, probably largely through the composition of the soil air and organic matter changes.

Further work should be done on the effects of different types of cultivation. The evidence in this experiment is not decisive enough to warrant definite conclusions. It may be that on these soils the weed factor is not the only one which makes cultivation necessary.

The results of these studies indicate a need for more knowledge concerning the application of fertilizers. In other localities the subsurface application of fertilizers has proved beneficial by causing the plants to root deeper into the soil. This is especially important if the surface soils tend to dry out readily.

Finally, observations of corn root systems indicate that there is a wide diversity among the different varieties. Even within one variety the root systems of individual plants may be quite different. Hence, a study of the root systems of selfed lines of corn should be very beneficial in producing superior strains.

SUMMARY

Observations of the root systems of white potatoes, red clover, and corn were made during 1930 and 1931 with the purpose of determining the relations between the various soil characteristics and root development.

The root systems of all the plants studied were very much less extensive than those reported in the sub-humid and semi-arid regions of the western and mid-western states. Potato roots were limited to the first foot of soil, and lateral extent was seldom greater than 1 foot. The root systems of red clover did not penetrate farther than 3 feet even under the most favorable conditions. Corn roots extended no farther than 2 feet either laterally or vertically.

The soil acidity, per cent of organic matter, pore space, and soil texture apparently have little influence on root extension, although the pore space may be important in seasons of high rainfall.

The evidence indicates that the amount of soil moisture, at the time of seeding, influences the form of clover root systems to a large degree. Also the ample rainfall in this region seems to give plant roots very little stimulus to penetrate to the lower soil layers.

Coupled with the influence of soil moisture is the supply of mineral nutrients. Large amounts of commercial fertilizers are used in this region and most of this fertilizer is concentrated in the surface soil. Therefore plants are not provided with the necessary stimulus to develop extensive root systems.

The higher yields of white potatoes from small seed pieces spaced close together are apparently due to the more extensive utilization of the soil by the plant roots.

Different fertilizer ratios apparently had little effect on potato root systems. Differences were noted in the yields but this may be due to the direct influence of the fertilizer on the translocation of food to the tubers.

Various varieties of corn present quite different root systems. In general, the plants with the largest top growth had the most extensive root systems.

The differences in yields and root development of corn receiving different types of cultivation were very slight, and the evidence obtained is not conclusive enough to warrant recommendations. It is possible that the weed factor may not be the only one which makes cultivation necessary.

Additional problems suggested for investigation are: (*a*) the influence of micro-organisms on root development; (*b*) further studies on methods of cultivation; (*c*) the influence of the depth of fertilizer application on root development; and (*d*) studies of the root systems of selfed lines of corn and hybrids of these lines.

REFERENCES

(1) Bose, R. D., and Dixit, P. D. 1931 Studies in Indian barleys: II. The root system. *Indian Jour. Agr. Sci.* 1: 58–59 (Abst. in *Exp. Sta. Rec.* 66: 326).

(2) Bouyoucos, G. J. 1930 A comparison of the hydrometer method and the pipette method for making mechanical analysis of soils, with new directions. *Jour. Amer. Soc. Agron.* 22: 747–751.

(3) Bray, R. H. 1932 A test for replaceable and water-soluble potassium in soils. *Jour. Amer. Soc. Agron.* 24: 312–316.

(4) Brown, B. A. 1924 Spacing of potato hills. *Storrs Agr. Exp. Sta. Bul.* 119.

(5) Bryan, O. C. 1923 Effect of reaction on growth, nodule formation and calcium content of alfalfa, alsike clover and red clover. *Soil Sci.* 15: 23–35.

(6) Cannon, W. A. 1912 Physical relations of roots to soil factors. *Carnegie Inst. Wash. Yearbook* 11: 61–62.

(7) Cannon, W. A. 1918 Modification of root habits by experimental means. *Carnegie Inst. Wash. Yearbook* 17: 83–85.

(8) Cannon, W. A. 1921 Root growth in relation to a deficiency of oxygen or an excess of carbon dioxide in the soil. *Carnegie Inst. Wash. Yearbook* 20: 48–51.

(9) Cannon, W. A. 1924–25 Experimental studies on roots. *Carnegie Inst. Wash. Yearbook* 24: 289–298.

(10) Cannon, W. A. 1925–26 Studies on roots. *Carnegie Inst. Wash. Yearbook* 25: 317–325.

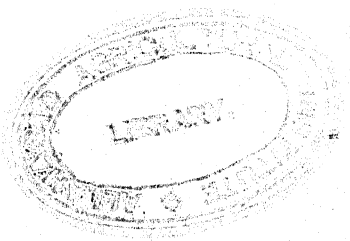
(11) Cannon, W. A. 1932 On the variation of the oxygen content of cultural solutions. *Science* 75: 108–109.

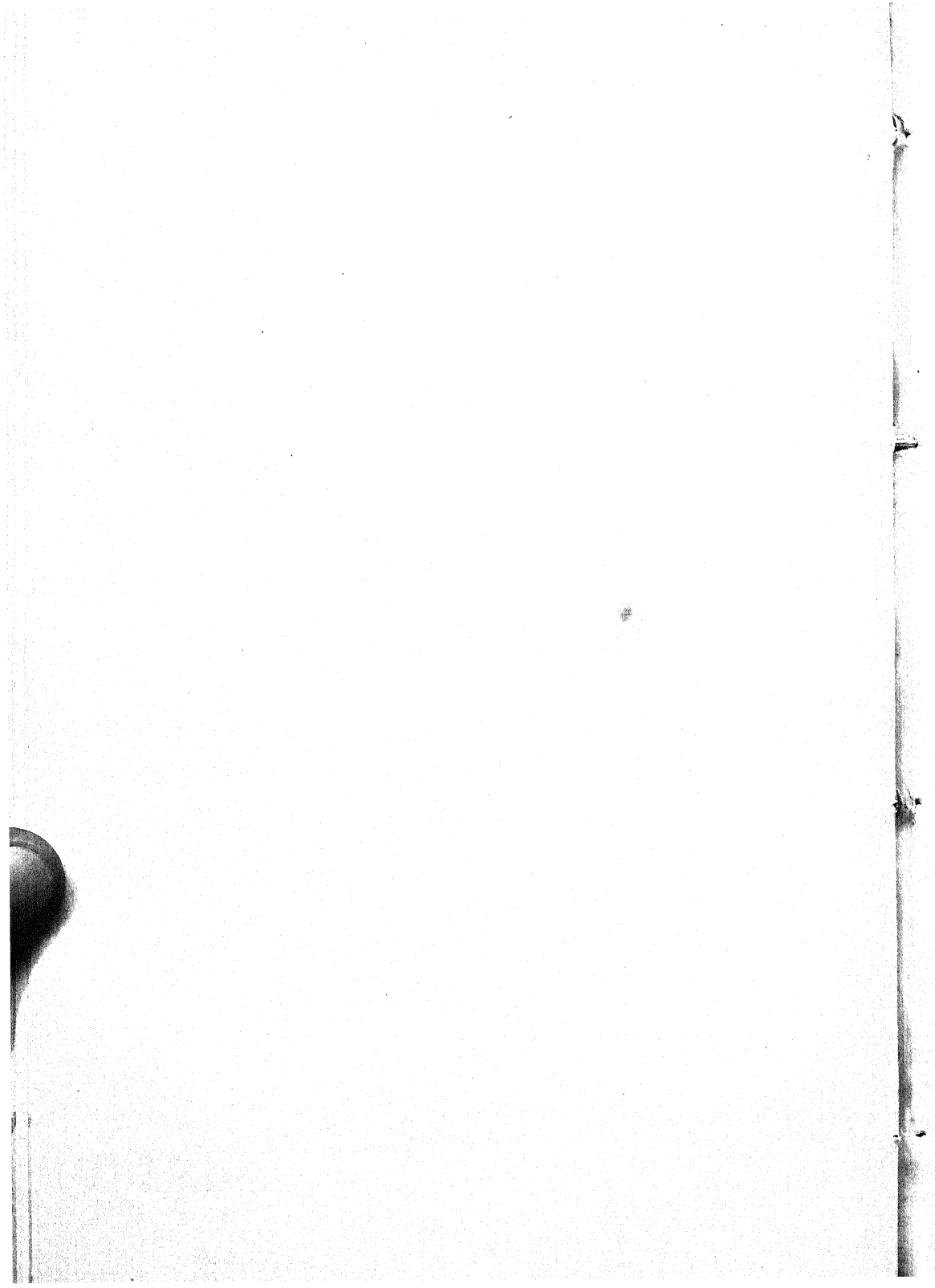
(12) Cates, J. S., and Cox, H. R. 1912 The weed factor in the cultivation of corn. U. S. Dept. Agr. Bur. Plant Indus. Bul. 257.

(13) Degtjareff, W. T. 1930 Determining soil organic matter by means of hydrogen peroxide and chromic acid. *Soil Sci.* 29: 239–245.

(14) EAMES, A. J., AND MACDANIELS, L. H. 1925 An Introduction to Plant Anatomy. McGraw-Hill, New York.
(15) GEORGESON, C. C., BURTIS, F. C., AND OTIS, D. H. 1897 Experiments with corn. Kans. Agr. Exp. Sta. Bul. 64.
(16) HENDRICKSON, A. H., AND VEIHMEYER, F. J. 1931 Influence of dry soil on root extension. *Plant Physiol.*, 6: 567–576.
(17) HILL, H. H. 1919 A comparison of methods for determining soil acidity and a study of the effects of green manures on soil acidity. Va. Agr. Exp. Sta. Tech. Bul. 19.
(18) HUTCHESON, T. B., HODGSON, E. R., AND WOLFE, T. K. 1917 Corn culture. Va. Agr. Exp. Sta. Bul. 214.
(19) LEBEDEV, A. F. 1928 The volume weight of soils as a physical characteristic of the soil profile. *Soil Sci.* 25: 207–211.
(20) LYON, T. L., AND BUCKMAN, H. O. 1926 The Nature and Properties of Soils. MacMillan, New York.
(21) LYON, T. L., AND WILSON, J. K. 1921 Liberation of organic matter by roots of growing plants. N. Y. (Cornell) Agr. Exp. Sta. Mem. 40.
(22) MARTIN, W. H., BROWN, B. E., AND SPRAGUE, H. B. 1931 The influence of nitrogen, phosphoric acid and potash on the number, shape and weight of potato tubers. *Jour. Agr. Res.* 43: 231–260.
(23) MILLAR, C. E. 1925 Availability of nutrients in subsoils. *Soil Sci.* 19: 275–285.
(24) MILLER, E. C. 1916 The root systems of agricultural plants. *Jour. Amer. Soc. Agron.* 8: 129–154.
(25) MORGAN, M. F. 1930 A simple spot plate test for nitrate nitrogen in soil and other extracts. *Science* 71: 343–344.
(26) MORROW, G. E., AND HUNT, T. F. Field experiments with corn. *Ill. Agr. Exp. Sta. Bul.* 4: 113–115 (1889); 8: 263–266 (1890).
(27) PARTRIDGE, N. L., AND VEATCH, J. O. 1932 The relationship between soil profile and root development of fruit trees. *Mich. Agr. Exp. Sta. Quart. Bul.* 14: 200–207.
(28) SCHREINER, O., AND SKINNER, J. J. 1918 The triangle system for fertilizer experiments. *Jour. Amer. Soc. Agron.* 10: 225–249.
(29) SEWELL, M. C. 1919 Tillage: A review of the literature. *Jour. Amer. Soc. Agron.* 11: 269–290.
(30) SMITH, A. M., AND ROBERTSON, I. M. 1931 The influence of the plant upon seasonal changes in soil acidity. *Jour. Agr. Sci.* 21: 822–831.
(31) SMITH L. H., AND WALWORTH, E. H. 1926 Seminal root development in corn in relation to vigor of early growth and yield of crop. *Jour. Amer. Soc. Agron.* 18: 1113–1120.
(32) SPRAGUE, H. B., AND EVAUL, E. E. 1929 Effect of size of seed piece and rate of planting on yields of white potatoes. *Jour. Amer. Soc. Agron.*, 21: 513–523.
(33) SPRAGUE, H. B., EVAUL, E. E., REUSZER, H. W., AND FARRIS, N. F. 1930 Experiments with alfalfa, clover and timothy for hay in New Jersey. N. J. Agr. Exp. Sta. Bul. 512.
(34) SPRAGUE, H. B., AND FARRIS, N. F. 1931 The effect of uniformity of spacing seed on the development and yield of barley. *Jour. Amer. Soc. Agron.* 23: 516–533.
(35) THOMAS, M. D. 1928 Soil structure as influenced by mechanical treatments and soluble salts. *Soil Sci.* 25: 409–418.
(36) THOMPSON, H. C. 1921 Effects of cultivation on soil moisture and on yields of certain vegetables. *Proc. Amer. Soc. Hort. Sci.* 1920: 155–161.
(37) TRUOG, E. 1916 The utilization of phosphates by agricultural crops. Wis. Agr. Exp. Sta. Res. Bul. 41.
(38) TRUOG, E. 1930 The determination of the readily available phosphorus of soils. *Jour. Amer. Soc. Agron.* 22: 874–882.

(39) TURNER, T. W. 1922 Studies of the mechanisms of the physiological effects of certain mineral salts in altering the ratio of top growth to root growth in seed plants. *Amer. Jour. Bot.* 9: 415–445.
(40) WAKSMAN, S. A. 1927 Principals of Soil Microbiology. Williams & Wilkins, Baltimore.
(41) WEAVER, J. E. 1926 Root Development of Field Crops. McGraw-Hill, New York.
(42) WEAVER, J. E., AND BRUNER, W. E. 1927 Root Development of Vegetable Crops. McGraw-Hill, New York.
(43) WOLFANGER, L. A. 1930 The Major Soil Divisions of the United States. Wiley and Sons, New York.





APPLICATION OF THE THEORY OF PROBABILITY TO THE SIZE DISTRIBUTION OF SOIL AGGREGATES[1]

CLARK AFFLECK[2]

Utah Agricultural Experiment Station

Received for publication September 5, 1933

In the study of mechanical analysis of soils extreme care is taken to obtain size-distribution curves of the various soils. These curves give a real picture of how the soils are made up mechanically. A crude example of a size-distribution curve may be described somewhat as follows:

Suppose a large number of small boxes of uniform width are placed side by side to form a long row, numbered from left to right with consecutive integers 1, 2, 3, 4, etc. Imagine a soil or some other finely divided substance graded according to size of particle, and the extremely small particles placed in the first box, those larger in radius by a small definite amount placed in the second, and so on, until extremely large particles are placed in the last box to the right. Let a vertical line be erected from the center of each box with a length proportional to the weight of material within the box from which it is drawn, and a smooth curve drawn through the end points of all the lines. It is natural to expect a humpbacked curve or one that touches the axis of abscissas where it has small and large values, and has one or more maxima at intermediate points. This actually has been found to be the case with soils.

An interesting problem arises: What is the most probable distribution when a given amount of some homogeneous substance is broken into fine particles by a random process? To attempt an answer to this question it will be necessary to make use of the theory of probability to develop an algebraic expression for the distribution. The particles will be classified in the order of increasing radius and will be identified with the various intervals which are one unit wide.[3]

If N is the total number of particles and N_r the number of particles identified with any particular radius interval corresponding to the discontinuous variable r, which is the average radius of the particles within an interval r_a to r_b,

$$\Sigma N_r = N. \qquad (A)$$

The fractional number of all the particles that are associated with any one radius interval may be defined by the equation

[1] Contribution, physics department, Utah Agricultural Experiment Station. Publication authorized by director, August 30, 1933.

[2] Graduate student.

[3] The following discussion to and including equation (R) is taken essentially from Arthur Haas' "Introduction to Theoretical Physics," vol. 2.

$$w_r = \frac{N_r}{N} \tag{B}$$

It must follow that

$$\Sigma w_r = 1. \tag{C}$$

Written in the general form the statistical probability of a distribution is expressed by the equation

$$W = \frac{N!}{N_1!\, N_2! \cdots N_r! \cdots} \tag{D}$$

where N_1, N_2, ... N_r, ... are the numbers of particles contained in the respective radius intervals, characterized by the subscripts. This expression can be greatly simplified and made more accessible to calculation by writing it in the logarithmic form, by the use of Stirling's formula, which is:

$$\log_e (n!) = n \log_e n - n + 1/2 \log_e (2\pi n).$$

For large values of n the last term is obviously small compared with the others, and the equation may be written

$$\log_e (n!) = n \log_e n - n. \tag{E}$$

Taking the logarithm of (D) and using (E),

$$\log_e W = N \log_e N - N - \Sigma N_r \log_e N_r + \Sigma N_r.$$

Using (A) and (B),

$$\log_e W = N \log_e N - \Sigma N w_r (\log_e N + \log_e w_r),$$

or

$$\log_e W = N \log_e N - N \log_e N \Sigma w_r - N \Sigma w_r \log_e w_r.$$

Finally by using (C)

$$\log_e W = - N \Sigma w_r \log_e w_r. \tag{F}$$

A given volume V of material is to be broken into a given number of particles N and distributed in such a way that the statistical probability W has a maximum value. These conditions may be stated mathematically by:

$$\delta W = 0, \quad \text{or} \quad \delta(\log_e W) = 0. \tag{G}$$

$$\delta N = 0. \tag{H}$$

$$\delta V = 0. \tag{I}$$

In accordance with (B) and (C), the constancy of the total number of particles may be written

$$\Sigma \delta w_r = 0. \tag{J}$$

If V_r is the volume of a single particle whose radius is characterized by the index r,

$$V = \Sigma N_r V_r \tag{K}$$

and

$$\delta V = \Sigma V_r \delta N_r. \tag{L}$$

By (I) the left-hand side of (L) is zero. Using (B), (L) may be rewritten

$$\Sigma V_r \delta w_r = 0. \tag{M}$$

This expresses the constancy of the total volume V.

By taking the variation of (F).

$$\delta(\log_e W) = -N\Sigma \log_e w_r \delta w_r - N\Sigma\delta w_r. \qquad (N)$$

The left-hand side is zero by (G) and the last term vanishes by (J); and since N cannot be zero the constancy of the probability may be written

$$\Sigma \log_e w_r \delta w_r = 0. \qquad (O)$$

In order to obtain a solution for w_r that will satisfy the three equations (J), (M), and (O), undetermined constants will be multiplied by each of equations (J) and (M) and the equations then added to equation (O), thus

$$\Sigma(\log_e w_r + \lambda_1 V_r + \lambda_2)\delta w_r = 0 \qquad (P)$$

where equation (M) is multiplied by λ_1 and (J) by λ_2. As the variation δw_r in general is arbitrary the equation can be satisfied only when the quantity in the brackets vanishes, thus

$$\log_e w_r = -\lambda_2 - \lambda_1 V_r$$

or

$$w_r = e^{-(\lambda_2 + \lambda_1 V_r)}. \qquad (Q)$$

Introducing two new factors $\lambda_1 = 1/\theta$ and $\lambda_2 = \psi/\theta$ (Q) becomes[4]

$$w_r = e^{(\psi - V_r)/\theta}. \qquad (R)$$

Substituting the value for w_r from (B)

$$N_r = NCe^{-(V_r/\theta)}. \qquad (S)$$

where $C = e^{\psi/\theta}$. Now $V_r = 4/3\ \pi r^3$ giving

$$N_r = NCe^{-(4/3\pi r^3)/\theta}. \qquad (T)$$

Multiplying both members by $4/3\ \pi r^3\rho$ where ρ equals the density of the material used,

$$4/3\pi\ r^3\rho N_r = NC\ (4/3\pi r^3\rho)\ e^{-4/3\pi r^3)/\theta}. \qquad (U)$$

The quantity on the left is the mass of the material in the radius interval corresponding to r which will be denoted by q_r. The quantity on the right can be simplified by introducing two more constants $A = 4/3\ \pi\rho NC$ and $E = e^{-(4/3\pi)/\theta}$.

Thus (U) becomes

$$q_r = Ar^3E^{-r^3}. \qquad (V)$$

In this equation r is a discontinuous variable having only integral values. If this expression is plotted in histogram fashion and a smooth curve passed through the points (r, q_r) the subscript may now be dropped and the continuous function

$$q = Ar^3E^{-r^3}. \qquad (W)$$

will approach the histogram in form as the radius intervals become extremely small.

The constant θ is as yet undetermined. By taking the derivative of (W) with respect to r and equating it to zero it is found that $[1 - r^3 \log_e E]$ must equal zero at the curve maximum or

$$r^3 = 1/\log_e e^{(4/3\pi)/\theta} = \theta/(4/3\pi). \qquad (X)$$

$$\theta = 4/3\ \pi\ r_m^3.$$

[4] The distribution that corresponds to this equation is known as "Gibbs' canonical ensemble."

Where r_m is defined as the value of r where the curve has its maximum ordinate q. Thus,

$$E = e^{(4/3\pi)/\theta} = e^{1/r_m^3}.$$

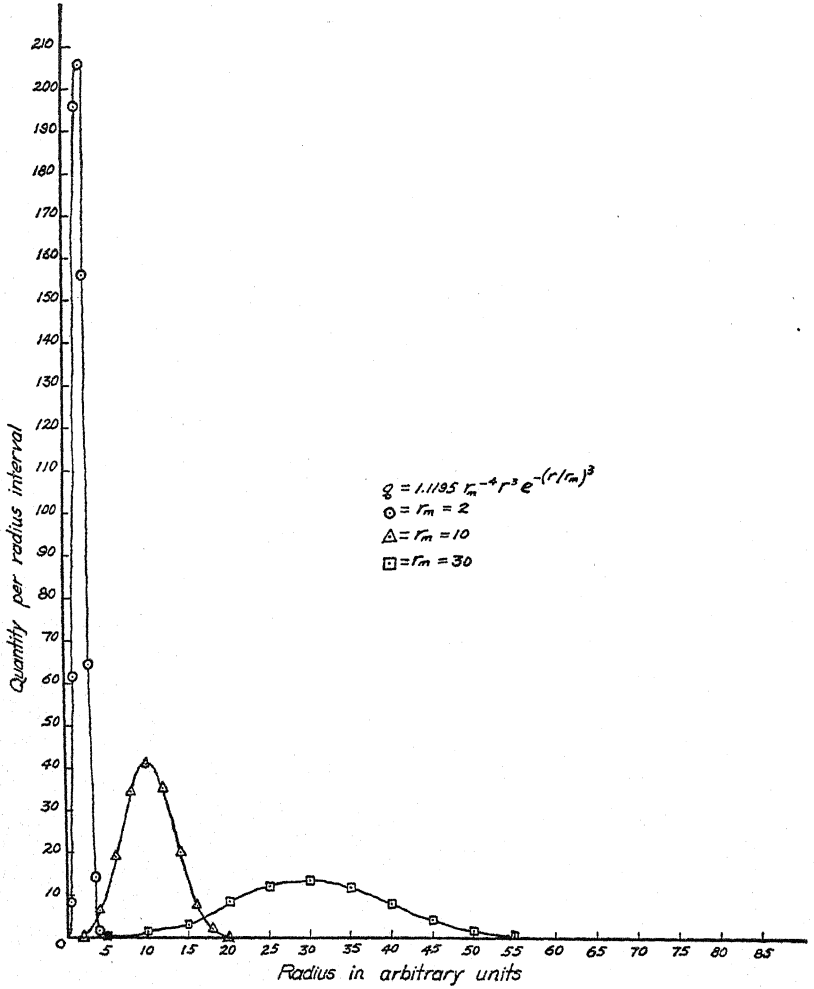


FIG. 1. GRAPHS OF DISTRIBUTION FUNCTION WITH THREE DIFFERENT VALUES OF r_m

And equation (*W*) becomes

$$q = Ar^3e^{-(r/r_m)^3}. \qquad (Y)$$

It is obvious that the area under the curve of (*Y*) is equal to the mass *M* of the material used.

By integration it is found that

$$M = Ar_m^4\,\Gamma(4/3)$$

or[5]

$$A = M/r_m^4\,\Gamma(4/3). \qquad (Z)$$

If M is made equal to unity $A = 1.1195\,r_m^{-4}$, which leads to an equation with one parameter.

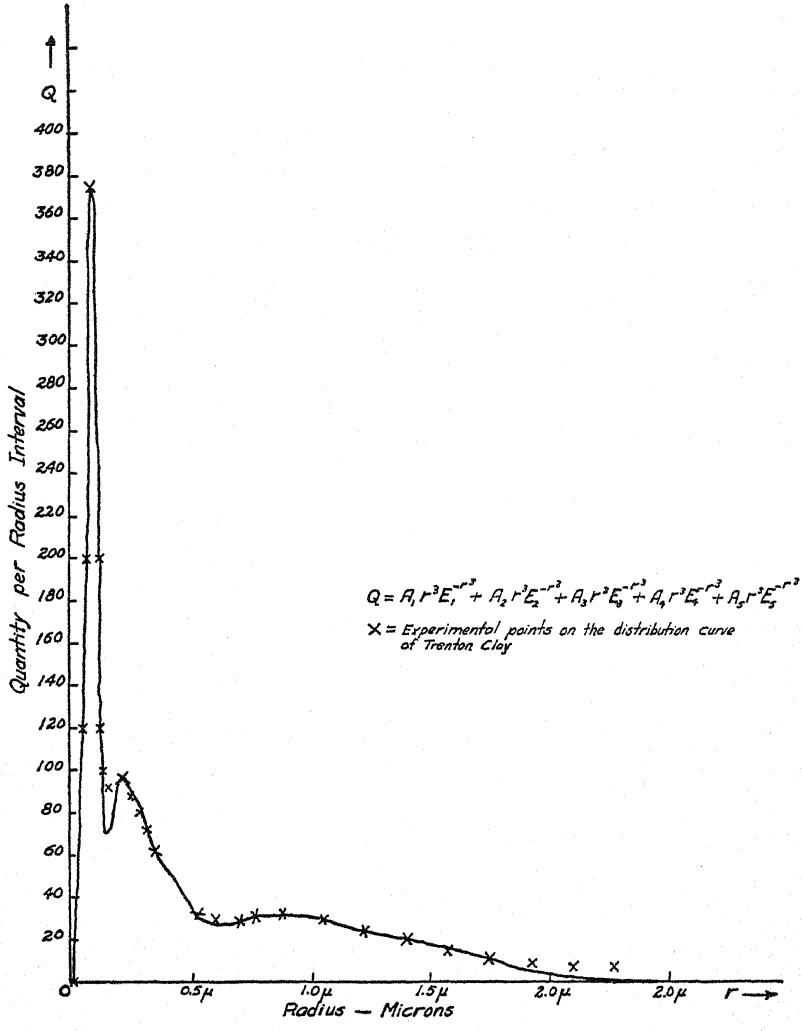


FIG. 2. COMPARISON BETWEEN THEORETICAL SYNTHETIC CURVE AND EXPERIMENTAL RESULTS

$$q = 1.1195\,r_m^{-4}\,r^3 e^{-(r/r_m)^3} \qquad (AA)$$

This equation is an expression for the most probable distribution that may

[5] $\Gamma(4/3)$ is the Gamma function of (4/3).

$$\Gamma(n) \equiv \int_0^\infty x^{(n-1)}\,e^{-x}dx.$$

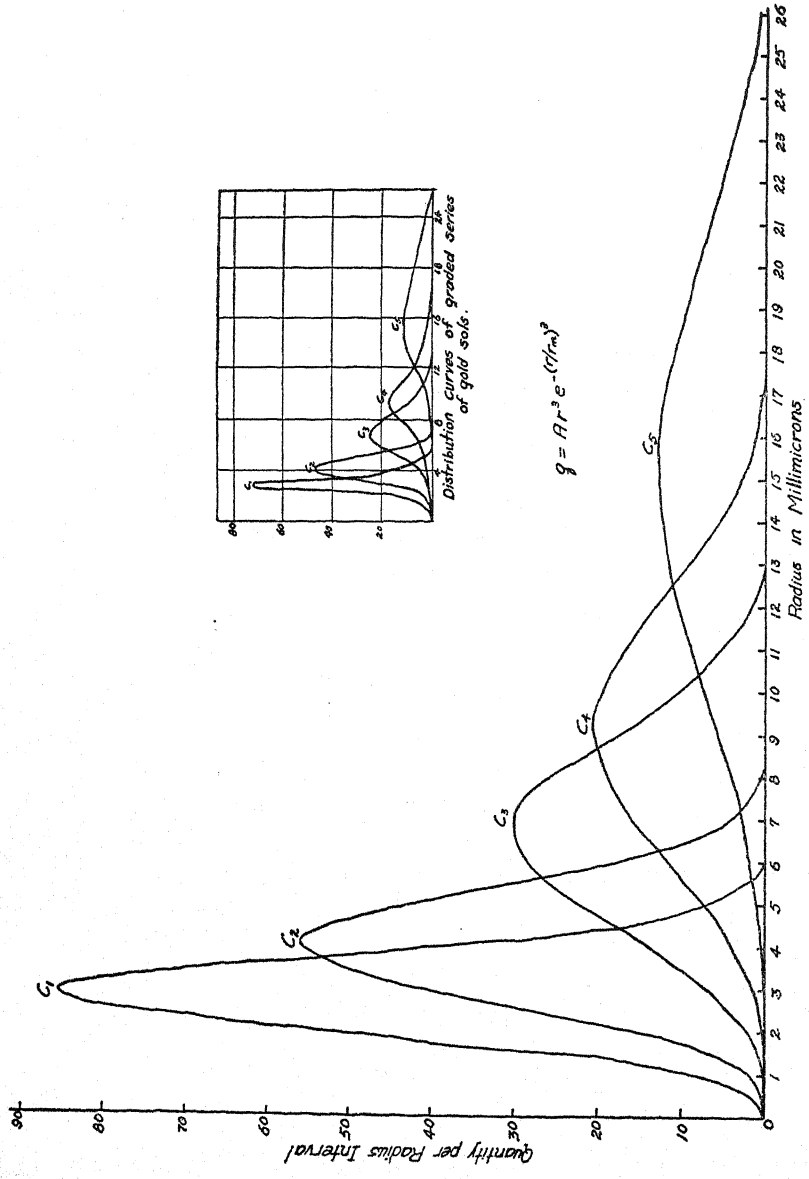


FIG. 3. THEORETICAL DISTRIBUTION CURVES OF GOLD SOLS SHOWN IN INSET

arise when a unit quantity of a homogeneous material is broken into small particles by a random process.

Figure 1 presents three plots of the expression with different values for r_m.

It is apparent that none of these curves in general would fit soil-distribution curves. In the case of soils, however, it must be remembered that instead of being composed of a homogeneous material there are several kinds of material with different physical properties each of which has a distribution curve of its own. For an example of this, a distribution curve of Trenton clay[6] is presented by the crosses in figure 2.

By summing several terms of the type given in equation (Y) resulting in an equation of the form

$$q_1 + q_2 \ldots + q_n = A_1 r^3 e^{-(r/rm)^3} \ldots + A_n r^3 e^{-(r/rm_n)^3} \qquad (BB)$$

it should be possible to fit approximately this curve. In order to do this it seemed convenient to select the r_m's, then solve for the A's by introducing as many linear equations as there are r_m's, these equations being obtained by passing the curve through the points

$$(r_{m_1}, Q_1), (r_{m_2}, Q_2), \ldots (r_{m_n}, Q_n)$$

where $Q_1, Q_2, \ldots Q_n$ etc., equal the ordinates of the experimental curve with the respective abscissas $r_{m_1}, r_{m_2} \ldots r_{m_n}$.

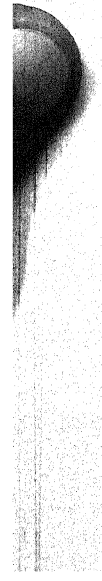
Figure 2 shows that there are three noticeable maxima. By passing the theoretical curve through these three points, thus letting $n = 3$ and then subtracting this curve from the experimental curve, two new maxima are obtained. Using these and repeating the above process with $n = 5$ a close fit results which is shown by the solid line in figure 2. It is clear that by adding subsequent minor distributions a more precise fit may be obtained.

The two sets of curves presented in figure 3 illustrate how (Y) may represent the experimental facts when only one material is distributed. The inset curves are distributions of a series of graded gold sols obtained by Rhinde.[7] The other curves are plots of (Y) with the constants chosen so as to make the r_m's the same as in the experimental distributions and the ordinates of the maxima proportional.

It would seem, therefore, that a consideration of the theory of probability leads to a rational equation representing distribution curves of dispersed materials.

[6] JENNINGS, D. S., THOMAS, M. D., AND GARDNER, W. 1922 A new method of mechanical analysis of soils. *Soil Sci.* 14: 485–499.

[7] NICHOLS, J. B. 1932 *The ultracentrifuge and its field of research. Indus. and Engin. Chem.* (Analyt. Ed.) 4: 12–17. *Original Reference:* RHINDE 1928 Distribution of Sizes of Particles in Gold Sols, p. 145–165 Dissertation (Upsala, Sweden). (Not seen.)



THE CARBON-NITROGEN RATIO IN RELATION TO SOIL CLASSIFICATION

M. S. ANDERSON AND HORACE G. BYERS

Bureau of Chemistry and Soils, U. S. Department of Agriculture

Received for publication August 29, 1933

In a recent bulletin (4) the writers have called attention to the marked differences in the properties of organic matter derived from podzols and from prairie and other dark colored soils. They have also (10) called attention to the relationship between the chemical properties of the inorganic soil colloids and the great soil groups, as developed by Marbut and his co-workers (18, 19), in the study of the field characteristics of soils. This relationship has been more fully developed for the inorganic colloids in subsequent publications (6, 7, 9).

It is of great interest to ascertain whether the organic colloid of soils is likewise differentiated by climatic influences and is a variable material, not only in quantity but in character in different soils. The analytical data on the organic matter of soils is very meager except in two respects: the carbon content of the soil and the nitrogen content. The determination of these two components is relatively easy and with proper precautions may be very exact, and many reports are available which deal with them. The value of many of these is greatly lessened, for our present purpose, by reason of the apparent impossibility of differentiating between charcoal and coal particles and soil organic matter, and because but few of the investigations have been so carried out that horizontal differentiation can be considered. It seems probable also that some of the carbon determinations have been reported without due attention to the possible presence of carbonate. Soil classification is based upon profile characteristics and not alone on surface soil. It seemed probable, however, that sufficient usable data are available to ascertain whether the carbon-nitrogen ratio reveals any soil group characteristics.

This ratio has long been considered an important characteristic. Indeed, it was for a time, and apparently by some still is, considered sufficiently constant so that the nitrogen determination may serve as a means of estimating the organic content of a soil (16).

This assumption has repeatedly been shown to be invalid (15) and its use undoubtedly persists because within limited areas it has been found that the ratio is fairly constant for surface soils. Indeed, G. W. Robinson (22) in his text book says, on page 136, "The organic matter of soils contains carbon and nitrogen in the approximate ratio of 10:1" and on page 142, "For the soils of

the temperate regions the ratio approaches very closely 10:1." It is true that he also states, on page 352, "As a measure of soil organic matter it [the determination of nitrogen] is highly untrustworthy. It may yet prove a valuable aid to the definition of soil groups." Jenny (11) states that the ratio widens with decreased temperature and narrows with increase of temperature. He gives a range between 9:1 and 13:1. McLean (18), on the other hand, finds the ratio much higher in certain tropical soils than in England. An average of 11 tropical soils shows a ratio of 15.2 with a range between the limits of 23.0 and 9.0, while 43 English soils have a mean ratio of 9.7. It would appear, therefore, that an examination of existing data might be useful for general purposes as well as to determine whether those conditions which produce the differentiation shown by the great soil groups also produce a recognizable variation in the carbon-nitrogen ratio.

EXPERIMENTAL DATA

Before entering upon a critical examination of the data presented in the following tables attention must be directed to a few considerations concerning the determinations themselves and the resulting ratios. In the determination of organic carbon there are a number of uncertainties which materially affect the results. It is known that the carbon-nitrogen ratio of plant residues is very variable and may be as high as 80, and even in nitrogen-rich material, such as legumes, is about 20. In the determination of the soil carbon it is often uncertain how much of this undecomposed material is present and it is certainly clear that such material is not *soil* organic matter in the ordinary sense. In making carbon determinations it is customary to neglect any carbon dioxide arising from carbonates except when fairly large quantities are present, yet it has been shown (1) that rather appreciable quantities of carbon dioxide are present even in acid soils. Even when present in large quantities the methods used for its determination, while sufficiently accurate for most purposes, are still inexact enough to make the correction employed for carbon sufficiently uncertain to make material differences in the carbon-nitrogen ratio. The determinations cited in the following are made without reference, in many cases, to horizons, and therefore the differences shown by "soil" and "subsoil" are not as great as probably exist between A and B horizons. Although some investigators have considered only virgin soils, in most cases cultivated areas have been studied with the primary purpose of determining the effect of cultivation upon the organic soil content. In many cases it is not known whether virgin or cultivated soils are reported. No attempt is therefore made to segregate the data on this basis. It may be noted, however, that the work of Sievers (25) and others shows that uniform cultural treatment of soils tends to diminish the variation of the carbon-nitrogen ratio.

Finally, it is to be noted that as a given profile deepens the organic matter and nitrogen both decrease in quantity and in many cases the unavoidable experimental errors mask the relations sought. With these considerations in

mind it will be seen that any general relations shown by the data given in the following have an added interest.

The Chernozem soils

The data selected to show the carbon-nitrogen ratio for Chernozem soils are collected from various publications, as indicated in table 1, and from certain unpublished data on file in the Division of Soil Chemistry and Physics. It is probable that some of these profiles are really developed in areas more arid than correspond to true chernozem soils but it is believed that no serious error is made by their inclusion. Only soils are included from which more or less definite profile data may be obtained.

Since in part the samples included in table 1 were examined analytically for purposes quite different from that of the present study, and some of them are not subdivided by horizons and others present subdivisions of horizons, it is difficult to summarize the results in a manner not open to criticism. If, however, we select all values for samples which are wholly above 10 inches in depth, and arbitrarily take the average of these as the average ratio for the topsoil, we obtain a ratio of 9.0, with a maximum of 10.9 and a minimum of 7.5. This degree of constancy is very remarkable in view of the wide variation in carbon content. For the next layer of soil which lies between a minimum and a maximum depth 5 to 20 inches the mean value is 7.6, with a maximum of 9.3 and a minimum of 5.3. For the next layer, at depths ranging from 18 to 40 inches, the mean ratio is 6.7 with a maximum of 9.4 and a minimum of 3.9. The ratios below these depths, and indeed some of those above them, have qualitative significance only since the quantities of both nitrogen and carbon are so small that no great reliance can be placed upon the quantities reported. They do indicate, however, that the ratio is very low and decreases progressively with depth.

Because of the probable presence of undecomposed organic matter in the surface of most soils a more satisfactory comparison of the carbon-nitrogen ratios could doubtless be obtained from the colloid analyses except that in most cases ammonia has been used as a dispersing agent and the colloid acids retain ammonia when the colloid is dried. Most colloid data are therefore useless for the present purpose. In some recent work by I. C. Brown of this bureau chernozem colloids were extracted by the use of distilled water only. Table 1a contains the carbon-nitrogen ratios calculated from these analyses (7).

The profiles given in table 1a were collected from virgin soils and were subdivided to a greater degree than is usual in soil studies. They represent a series of soils in Nebraska which are produced from the same parent material—loess. The Keith silt loam is classified as a chestnut brown soil rather than as a true chernozem. The Phillips sandy loam from Montana is a solonetz soil developed under low rainfall from glacial drift.

The mean value of the carbon-nitrogen ratio for those fractions of the profiles regarded as A horizons is 9.1; for the B horizons, including all layers of

TABLE 1

Carbon-nitrogen ratios of chernozem and related grassland soils

SOIL SERIES AND LOCATION	DEPTH	NITOGEN CONTENT	C:N RATIO	SOIL SERIES AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Colby silty clay loam, Kans. (21)	2–10	.15	10.9	Rocky Ford fine silt loam, Colo. (15)	0–8	.11	8.2
	10–20	.07	9.2		8–13	.08	7.9
	20–33	.04	9.4		13–24	.03	7.0
	33–47	.03	6.2		24–36	.03	6.3
	47–60	.03	2.8				
	60–72	.03	2.7	San Luis sandy loam, Colo. (15)	0–10	.70	7.5
					10–24	.50	5.3
					24–36	.30	4.2
Prowers clay, Colo. (15)	0–8	.14	9.1				
	8–18	.11	7.9	Jordan sandy loam, Utah (0)	0–10	.13	8.3
	18–24	.07	7.1		10–22	.07	6.5
	24–36	.05	7.2		22–36	.05	5.7
Prowers loam, Colo. (15)	0–9	.14	8.5	Crete silt loam, Nebr. (7)*	0–1½	.13	8.9
	9–18	.08	7.5		1½–4	.15	9.3
	18–36	.05	6.0		4–20	.17	7.5
					20–38	.10	5.2
Prowers clay loam, Colo. (15)	0–9	.16	8.0				
	9–20	.09	7.5	Hastings silt loam, Nebr. (7)*	0–6	.22	9.2
	20–36	.05	6.2		6–20	.15	8.5
					20–30	.08	4.4
Prowers clay loam, Colo. (15)	0–8	.15	9.0		30–43	.07	5.0
	8–18	.08	7.6				
	18–24	.06	5.3	Amarillo silty clay loam, Tex. (3)*	0–5	.13	9.0
	24–36	.04	7.1		10–20	.08	8.0
					30–40	.06	5.0
Prowers clay loam, Colo. (15)	0–8	.21	9.5	Fillmore silt loam, Nebr. (7)*	0–2	.33	9.5
	8–18	.09	8.3		2–6½	.21	8.0
	18–36	.08	3.9		6½–16	.12	5.8
Las Animas clay, Colo. (15)	0–8	.10	8.2	Holdrege silt loam, Nebr. (7)*	0–4	.22	9.2
	8–18	.07	8.1		4–7	.18	10.9
	18–24	.04	7.2		7–18	.15	9.3
	24–36	.04	7.2		18–30	.08	5.8
Manville silt loam, Colo. (15)	0–8	.10	8.8	Charbon loam, N. Dak.†	0–1½	.23	9.3
	8–18	.09	9.3		1½–5	.16	9.1
	18–36	.03	8.3		5–13	.10	5.7
Rocky Ford fine silt loam, Colo. (15)	0–8	.13	9.3				
	8–15	.11	7.4				
	15–36	.05	5.1				

* Carbon values calculated by taking 58 per cent of the organic matter content determined by H_2O_2.

† Unpublished data.

TABLE 1a

*Carbon-nitrogen ratios of colloids extracted from chernozem soils**

SOIL SERIES AND LOCATION	DEPTH	HORIZON	C†	N	C:N RATIO
	inches		*per cent*	*per cent*	
Fillmore silt loam, Nebraska	0–2	A_1	7.38	.70	10.5
	2–6½	A_2	4.42	.33	13.4
	6½–16	B_1	1.19	.14	8.5
	16–38	B_2	1.07	.12	8.9
	38–42	B_3	0.85	.12	7.1
	42–60	B_4	0.64	.13	4.9
	60–84	B_5	0.55	.08	6.9
	84–96	C	0.31	.07	4.4
Crete silt loam, Nebraska	0–1½	A_1	3.82	.42	9.1
	1½–4	A_2	4.16	.44	9.5
	4–20	A_3	3.86	.44	8.8
	20–38	B_1	1.32	.18	7.3
	38–60	B_2	0.64	.14	4.6
	64–84	C	0.53	.13	4.1
Hastings silt loam, Nebraska	0–6	A_1	4.17	.45	9.3
	6–20	A_2	3.42	.36	9.5
	20–30	B_1	1.36	.18	7.6
	30–43	B_2	0.86	.12	7.2
	43–57	B_3	0.59	.05	11.8
	57–78	B_4	0.50	.06	8.3
	78–108	C	0.63	.07	9.0
Holdrege silt loam, Nebraska	0–4	A_1	4.34	.51	8.5
	4–7	A_2	5.28	.55	9.6
	7–18	A_3	3.67	.41	9.0
	18–30	B_1	1.37	.16	8.6
	30–49	B_2	0.94	.17	5.5
	49–72	B_3	0.45	.12	3.8
	72–96	C	0.70	.13	5.4
Keith silt loam, Nebraska	0–½	A_1	3.09	.37	8.4
	½–3½	A_2	3.67	.48	7.6
	3½–14	B_1	3.29	.31	10.6
	14–21	B_2	1.73	.23	7.5
	21–33	5	0.97	.16	6.1
	33–40	6	1.02	.14	7.3
	40–48	7	1.08	.08	13.5
	48–72	8	0.74	.13	5.7
	72–96	9	0.52	.10	5.2
Phillips sandy loam, Montana	0–1½	A_1	5.97	.80	7.5
	1½–4	A_2	4.33	.59	7.3
	4–9	B_1	2.38	.35	6.8
	9–19	B_2	1.50	.21	7.1
	19–36	B_3	1.54	.20	7.7
	36–54	B_4	0.79	.11	7.2
	54–64	C	0.90	.11	8.2

* Data taken from a manuscript by Brown, Rice, and Byers (7).

† Carbon values calculated by taking 58 per cent of the values given for organic matter.

the Keith except the lowest, it is 7.5. The mean for the six C horizons is 6.1. These results are of great interest despite the rather wide variations in individual analyses. They demonstrate very clearly that the chernozem[1] normal carbon-nitrogen ratio is materially less than that of soils of the humid areas and that the ratio decreases with depth. The significance of these results will be considered in the general discussion (q.v.).

A further indication of the general character of the organic matter of colloids of the chernozem type is found in the colloid of the Colby silty clay loam of the Kansas erosion station (21). The ratios are 7.9 for 2 to 10 inches; 6.1 for 10 to 20 inches; 4.0 for 20 to 33 inches; and 3.4 for 33 to 47 inches.

Prairie soils

A large number of analyses of the carbon and nitrogen of soils of the prairie type are available. The greater number of those given in table 2 are taken from the work of Brown and O'Neal (8), whose analyses are reported in graphic form. The calculations made from the graphs are not strictly accurate to the first decimal place but are sufficiently accurate for the present purpose. Data for prairie soils are also available from Illinois, Missouri, and Nebraska.

A weighted average of the Iowa soils given in table 2 shows for the surface 7 inches a ratio of 12.2; for 7 to 20 inches, 11.5; and for 20 to 40 inches, 11.1. The two complete profiles from Bethany, Missouri, and Lincoln, Nebraska, show even more sharply the decrease in the ratio with increase in depth. Two very interesting profiles of prairie soils are not included in the table. One of these is the Marshall silt loam from the Erosion Experiment Station near Clarinda, Iowa (21). The carbon-nitrogen ratios for this soil are 9.8 for 0 to 13 inches, 10.2 for 13 to 24 inches, 7.9 for 24 to 45 inches, and 6.2 for 45 to 71 inches. This profile is from an area long cultivated and subjected to erosion. It offers an interesting example of an effect of erosion on organic matter. The other profile of special interest is a Palouse silt loam from the Erosion Experiment Station near Pullman, Washington. The Palouse soils are described by Marbut (19) and definitely classified as chernozem soils. Yet the analyses of the erosion station soil and its colloid reveal no chernozem characteristics as indicated by the silica ratios or carbonate accumulation, at least to a depth of 75 inches (21). The carbon-nitrogen ratios are, however, 9.7 for 0 to 20 inches, 4.6 for 20 to 33 inches, 5.3 for 33 to 62 inches, and 5.2 for 62 to 75 inches. These ratios are very distinctly of the chernozem type (*see* table 1). The corresponding ratios for the colloid are 6.9, 6.5, 4.8, 3.3, and 3.0, and those for the colloid of the Shelby soil profile given in table 2 are 9.3, 7.9, 4.9, 3.4, 4.1, and 5. It can not be concluded, however, that the carbon-nitrogen ratios are always smaller for the colloids than for the corresponding

[1] It is to be noted that tables 1 and 1a include soils which have developed under short grass cover and are not all true chernozems.

soils. The ratios for the colloid of the same Marshall silt loam profile cited in the foregoing for the soil are 10.4, 10.3, 7.3, and 6.8.

Podzol soils

There is not available at present a sufficient number of profile analyses of podzol soils to give a very definite estimate of the carbon-nitrogen ratios of the group. The material at hand is included in table 3.

In addition to these determinations, two series of podzols from Quebec

TABLE 2

Carbon-nitrogen ratios of prairie soils

SOIL SERIES AND LOCATION	DEPTH	C:N RATIO	SOIL SERIES AND LOCATION	DEPTH	C:N RATIO
	inches			*inches*	
Average of 9 profiles (8)	0–7	11.9	Average of 6 profiles (8)	0–7	11.9
Calhoun silt loam, Ia.	7–20	10.8	Waukesha loam, Ia.	20–40	12.9†
	20–40	10.1			
			Average of a group (26)	Surface	12.1
Average of 9 profiles (8)	0–7	13.3	of 83 silt loam soils of	Subsurface	11.5
Grundy silt loam, Ia.	7–20	12.8	Illinois	Subsoil	8.9
	20–40	11.5			
			Average of a group (26)	Surface	11.7
Average of 15 profiles (8)	0–7	12.1	of 16 black clay loam	Subsurface	11.9
Clinton silt loam, Ia.	7–20	10.5	soils of Illinois	Subsoil	9.0
	20–40	9.9			
			Shelby silt loam (21),	0–7	11.7
Average of 10 profiles (8)	0–7	12.3	Bethany, Mo.	8–12	11.4
Tama silt loam, Ia.	20–40	11.0		12–20	10.2
				20–24	6.8
Average of 4 profiles (8)	0–7	10.6		24–48	5.2
Marshall silt loam, Ia.*	20–40	8.4		48–60	4.1
Average of 6 profiles (8)	0–7	12.7	Soil profile (2) near Lin-	0–12	12.6
Muscatine silt loam, Ia.	20–40	10.5	coln, Neb.	12–24	12.5
				24–36	12.2
Average of 4 profiles (8)	0–7	12.7		36–48	10.0
Webster loam, Ia.	20–40	11.9		48–60	7.3
				60–72	5.2

* One of these samples differs widely from the others, being abnormally high in nitrogen.

† One of these subsoil samples is abnormally low in nitrogen.

Province, Canada, are reported by McKibbin and Gray (17). One series of "upland podzols," eight in number, give a mean carbon-nitrogen ratio of 21.4 for the surface soil and 19.3 for the subsoil. Another series of "lowland podzols," eleven in number, give a mean value for the surface soil of 22.6 and 21.1 for the subsoil. The variations in both series are between wide limits. In neither series are the depth measurements indicated. No data are available for the so-called "podzols" of the pedocal type (14) nor for ground water podzols.

Only one definite conclusion can be drawn from the data. Podzol soils have a much higher mean carbon-nitrogen ratio than have either chernozem or prairie soils. It appears probable that the variation with depth is less regular and that the processes which produce podzolization also produce this irregularity (*see* general discussion).

Gray-brown podzolic soils

A very large number of determinations of the carbon-nitrogen ratio of gray-brown podzolic soils are available; unfortunately, however, only a very limited

TABLE 3

Carbon-nitrogen ratios of podzol soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN§	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Caribou loam (15), Maine	0–8	0.23	13.2	Beckett loam* (3) Mass.	0–6	1.04	16.5
	8–12	0.14	10.9		6–11	0.05	23.2
	12–18	0.08	10.0		11–13	0.14	37.6
	18–36	0.07	7.0		13–24	0.09	36.1
					24–36	0.02	40.6
Superior fine sandy loam* (3), Wisc.	0–3	1.17	20.1				
	3–8	0.04	18.8	Lakewood soil series (13), N. J.†	0–5	0.016	48.3
	12–30	0.03	27.0		5–15	0.008	15.2
	30–40	0.01	11.6		15–23	0.023	23.8
					23–40	0.024	17.8
Lakewood soil series (13), N. J.†	0–2	0.103	40.8		40+	0.008	10.6
	2–8	0.009	87.7				
	8–10	0.041	32.4	Podzol profile from Connecticut, probably Brookfield loam; depths not given‡	A_0 "F"	1.69	28.2
	10–12	0.044	27.5		A_1 "H"	1.33	29.8
	12+	0.008	33.8		A_2	0.11	23.3
					B_1	0.27	27.5
				Washburn loam (14), Maine	0–8	0.32	15.3

* Ratio calculated from organic matter by H_2O_2 method.

† Some charcoal from forest fires present.

‡ Forest soil investigations in Connecticut. M. F. Morgan, *Amer. Soil Survey Assoc. Rept. 10th Ann. Meeting Bul.* 11: 108–114 (mimeographed).

§ Samples of podzol soils are sometimes taken after elimination of the leaf mould on the surface; in other cases the leaf mould is collected and labelled the A_0 horizon. In this table the high-nitrogen samples apparently consist largely of leaf mould.

number are of profile samples, and in many cases these are profiles of cultivated soils. It is impossible, therefore, to determine to what extent the surface horizons have been affected by erosion or fertilization. A selection of these profile samples is given in table 4. Because of the predominant number of profiles from the more southern members of the group, it is not believed that this selection fairly represents the soil group.

If a weighted average of these profiles be taken we find the ratio of the A horizon to be 12.5; that of the B horizons, 10.3; and of the C horizons, 7.6. It should be noted that the data of table 4 include averages for ten profiles of Norfolk soils and nine of Sassafras. Since the detailed data are not given, the interested reader is referred to the literature cited. If these references are consulted it will be found that the nine Sassafras profiles show a fair constancy, the range being between the limits of 9.6 and 13.8. On the other hand,

TABLE 4

Carbon-nitrogen ratios of gray-brown podzolic soil profiles, including red and yellow podzolic soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN CONTENT	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Berkshale loam (15), Pa.	0–8	.18	10.2	Sassafras loam (15), Md.	0–10	.13	9.6
	8–18	.09	9.2		10–20	.03	7.4
	18–36	.05	4.1		20–36	.02	6.8
Sassafras loam (15), Va.	0–8	.07	12.4	Sassafras series (15) average of 9 profiles	A horiz.	...	11.2
	8–15	.04	7.7		B horiz.	...	8.3
	15–36	.04	5.6		C horiz.	...	6.6
Norfolk fine sandy loam (15), Va.	0–9	.06	12.4	Norfolk sandy loam (15), S. C.	0–8	.03	18.1
	9–20	.02	7.6		8–30	.01	20.0
	20–36	.02	13.3		30–36	.03	8.0
Norfolk series (15) average of 10 profiles	A horiz.	...	16.3	Vernon fine sandy loam* (21), Okla.	0–3	.70	13.0
	B horiz.	...	12.3		3–10	.21	15.4
	C horiz.	...	9.1		10–27	.15	11.6
				Rossmoyne silt loam, Ohio†	0–8	.13	11.4
					8–16	.05	9.8
					16–20	.04	6.5
					22–24	.03	7.1

* These ratios are calculated from the H_2O_2 solution loss.

† Conrey, G. W., Steele, J. G., and Green, T. C. The composition of the Rossmoyne silt loam and its extracted colloid. *Amer. Soil Survey Assoc. Rept. 10th Ann. Meeting* Bul. 11: p. 1–14 (mimeographed).

the ten Norfolk profiles show highly variable ratios, the range being from 7.1 to 26.5 with values well distributed throughout this range.

To supplement the results given in table 4 the data given in table 4a are presented. These data, taken for the most part from a paper by Robinson and Holmes (23), give the surface soil and subsoil ratios. To these are added the data for two soils taken from the work of Leighty and Shorey (15).

The mean value of the ratio for the surface soils is 12.7 and for the subsoils

10.2 Although these ratios check closely with the averages for table 4, it is to be noted that the variations are extremely wide.

It is greatly to be regretted that no data are available for the colloids of this group. There are many analyses of colloids, but in every case except one the colloids were extracted with the aid of ammonia. This is the Vernon fine sandy loam from Oklahoma (21). In this profile the colloid has a C:N ratio for depth 0 to 3 inches of 7.1; for 3 to 10 inches, 5.6; for 10 to 27 inches, 3.7; and for 27 to 58 inches, 1.5. Whether in the other colloids a like low ratio would appear is unknown.

TABLE 4a

Carbon-nitrogen ratio of gray-brown podzolic surface soils and subsoils and certain red and yellow podzolic soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Chester loam (23), Va.	0–8	.07	17.4	Hagerstown loam (23), Md.	0–8	.13	6.6
	8–32	.03	15.1		8–30	.06	5.0
Clarksville silt loam (23), Ky.	0–10	.10	5.6	Manor loam (23), Md.	0–7	.11	10.8
	10–36	.04	12.3		7–20	.03	26.6
Huntington loam (23), Md.	0–8	.20	11.2	Ontario loam (23), N. Y.	0–12	.18	9.2
	8–30	.20	2.9		12–22	.04	8.7
Miami silty clay loam (23), Ind.	0–10	.09	10.6	Norfolk fine sandy loam (23), N. C.	0–8	.06	23.2
	10–24	.07	10.7		12–36	.04	5.7
Sassafras silt loam (23), Md.	0–8	.07	12.6	Marlboro sandy loam (15), N. C.	0–5	.055	18.0
	8–22	.03	8.6		12–18	.025	8.0
Portsmouth sandy loam (15), S. C.	0–8	.055	14.5				
	8–36	.027	8.9				

The lateritic soils

It should be noted that Marbut (10), in his former classification, does not recognize the existence of a lateritic great group, but, instead, he separates the soils of the southern humid area into yellow and red soils, which are podzolic in character in most cases. The examination of the colloids of these soils shows that some of them have silica-sesquioxide ratios of 2 or more. These we have included, so far as they are known, with the gray-brown podzolic soils in tables 4 and 4a, even though they may be yellow, as in the case of the Norfolk, or red, as in the case of the Vernon. The soils included in table 5 are either truly lateritic, with a silica-sesquioxide ratio for the colloids of below 2, or closely related to lateritic soils.

Table 5 shows no such wide variations in the carbon-nitrogen ratio as appear

in the podzol and podzolic groups. The mean value of the ratio for the A horizon is 15.2; for the B horizon, 10.8; and for the C horizon, 7.9. The high average of the surface soil is undoubtedly due to undecomposed organic matter.

TABLE 5

The carbon-nitrogen ratio of the lateritic group of soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	inches	*per cent*			*inches*	*per cent*	
Kirvin fine sandy loam (21), Tex.	0–12	.04	7.8	Nacogdoches fine sandy loam; Tex.*	0–8	.10	11.0
	12–24	.05	9.4		8–18	.06	11.0
	24–51	.02	7.0		18–40	.03	8.0
Cecil sandy clay loam (21), N. C.	0–6	.09	20.7	Cecil clay loam (23), Ga.	0–9	.03	10.8
	6–32	.04	6.5		9–18	.04	15.7
	32–60	.04	4.9				
Cecil sandy loam (15), N. C.	0–8	.03	17.3	Cecil fine sandy loam (15), N. C.	0–10	.04	13.6
	8–15	.03	13.3		10–18	.03	10.9
	15–36	.02	12.7		18–36	.02	6.6
Davidson clay loam (15), N. C.	0–7	.07	16.9	Greenville fine sandy loam (15), Ga.	0–8	.032	18.4
	7–12	.06	12.7		8–15	.032	13.7
					15–36	.026	8.4
Greenville sandy loam (15), Ga.	0–10	.036	15.2	Dunbar fine sandy loam (15), N. C.	0–8	.07	15.0
	10–15	.026	11.1		8–18	.02	8.0
	15–36	.023	7.4		18–36	.03	5.9
Appling sandy loam (15), N. C.	0–8	.04	21.1	Orangeburg fine sandy loam (23), Miss.	0–10	.03	14.9
	8–18	.03	12.6		10–36	.03	6.6
	18–36	.02	10.5				

* Unpublished data.

TABLE 5a

Carbon-nitrogen ratio of colloids from lateritic soils

SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO	SOIL TYPE AND LOCATION	DEPTH	NITROGEN	C:N RATIO
	ihches	*per cent*			*inches*	*per cent*	
Kirvin fine sandy loam (21), Tex.	0–12	.21	7.0	Cecil sandy clay loam (21), N. C.	0–6	.15	8.9
	12–24	.14	3.4		6–32	.07	2.2
	24–51	.11	1.9				

In at least one of the profiles, the Cecil sandy clay loam, visible fragments of pine needles were observed.

The colloid carbon-nitrogen ratios of two samples are available. These are given in table 5a.

No general observations can be made upon such scanty data but it is of

interest that these two colloids have a higher ratio in the soil than in the colloid of the surface horizon but the difference is much more marked in the Cecil than in the Kirvin. The lower horizons of the colloids also are sharply different from the soils.

Laterite soils

No data concerning true laterites are available for United States soils since no such soils exist, so far as is known. The only data from abroad which seem of value are furnished by McLean (18) and by Bennett and Allison (5). As previously stated, McLean reports the mean of 11 tropical soils as 15.2. Presumably these are, at least in part, laterites. The data of Bennett and Allison include the inorganic composition of the whole soil, and from this it is possible to estimate the degree of laterization from the silica content. The carbon-nitrogen ratio of the extensively laterized soils is noticeably variable. However, a group of six surface soils show a mean ratio of 15.0.

Nitrogen and carbon content

It will be noted that nearly all of the preceding tables give the nitrogen content of the soils reported. This is a matter of considerable interest, though not directly pertinent to the main purposes of the paper. An examination of the available data for the carbon content was also made. It can not be asserted that definite conclusions can be drawn. Variations within the groups are so wide as to very nearly mask group characteristics. Also, available data do not permit an estimate of the extent to which the quantities of carbon and nitrogen are affected by cultivation and erosion. It is known that, in general, cultivation decreases the organic content of soils. It is also known that the rate of this decrease is greatly influenced by climatic factors. The soils considered in this paper are partly virgin and partly cultivated. They also are from types of varying degrees of maturity. In many cases detailed information concerning the carbon content is not available and especially where horizontal data are given the horizons are not directly comparable. For these and other reasons there seems but little to be gained from attempting a detailed statement concerning the relative quantities of carbon and nitrogen.

It is of some interest to note the approximate averages of the carbon and nitrogen in the surface horizons of the great groups. These are shown in table 6.

It will be observed from the values given in table 6 that the differences among the great soil groups are very marked. The maximum content of both organic carbon and nitrogen is shown by the podzols. In this group also the average is derived from single values which are especially divergent. This wide divergence is probably due to the manner of collection of the samples. In some, the highly organic surface layer is included and in other cases is not. It seems probable that were this layer always included in the analytical data, the quantities would be more uniform and also higher. It is also true that the

organic content of the B horizon of the podzol soils is relatively very high. Whether this surface organic matter is included in the Canadian samples is unknown. The lowest carbon and nitrogen content shown in the table is for the lateritic group. It seems probable that were adequate data available the laterites would be still lower.

It seems probable that if *virgin* soils of the great soil groups were studied a more definite differentiation would appear. Especially would this be the case if the studies were made upon soils comparable in respect to maturity and to drainage conditions and with horizons properly segregated.

It is believed also that much information of value would be gained if future profile studies of both soil and colloid were so conducted as to throw additional light upon the relation between the organic content and the classification of soils. To make the best use of such data it is essential to know whether the

TABLE 6

Average carbon and nitrogen content of the surface soils of the great soil groups*

SOIL GROUP	ORGANIC CARBON	NITROGEN
	per cent	*per cent*
Chernozem	1.45	0.16
Prairie	2.50	0.20
Podzol (U. S.)	14.70	0.60
Podzol (Canadian upland)	3.30	0.15
Podzol (Canadian lowland)	5.40	0.25
Gray-brown podzolic	1.25	0.10
Lateritic	0.80	0.05

* It is to be noted the average carbon and nitrogen contents do not necessarily give a ratio which is the same as the average of the single ratios.

soils examined are virgin or cultivated and whether they have been modified by erosion or other processes likely to affect their organic content.

GENERAL DISCUSSION

In order to summarize the results given in the foregoing tables the mean values of the carbon-nitrogen ratio of the various groups are restated in table 7.

The values given in table 7 for the carbon-nitrogen ratio bring into sharp relief three points, of which two have already been emphasized by Leighty and Shorey (15). First, it is clearly evident that there is no constant ratio between nitrogen and organic carbon or total soil organic matter, either in soil or colloids. Second, the general relation is a decrease of the ratio, a relative increase of nitrogen, with increasing depth. Third, a wide divergence exists between the carbon-nitrogen ratio of the different great soil groups. Unfortunately, there is not adequate data to make certain how divergent the ratios may be within a soil series. It will be of interest to collect information upon this point, particularly from the colloids, when these are properly separated from the soil.

With respect to the first of these points little remains to be said except further to emphasize the point that however unsatisfactory the other methods of estimating soil organic matter (1) may be, certainly a determination of the nitrogen as a means of estimating carbon or organic content is about the worst, since the ratio not only varies widely from soil to soil but also varies with depth, and therefore with the degree of erosion. Whether there is also a seasonal variation is undetermined, but it seems probable. The chernozem soils, particularly the A horizon, appear to have an approximately constant ratio, though to what extent this is varied by cropping is not known. The prairie soils also have a fairly constant carbon-nitrogen ratio.

More is to be noted with respect to possible causes for the variation of the ratio with depth. The data of tables 1 to 5 show wide variations in this respect. Before general relations are considered it should be pointed out that as both carbon and nitrogen decrease in amount and the presence of small

TABLE 7

The mean carbon-nitrogen ratios of the great soil groups

GROUP	HORIZON A	HORIZON B	HORIZON C
Chernozem soils	9.0	7.6	6.7
Chernozem colloids	9.1	7.5	6.1
Prairie soils*	12.2	11.5	11.1
1 Prairie colloid	9.3	7.9	5.0
Podzol soils† (Canadian upland)	21.4	19.3	...
Podzol soils (Canadian lowland)	22.6	21.1	...
Podzolic soils	12.5	10.3	7.6
Podzolic soils	12.7	10.2	...
Lateritic soils	15.2	10.8	7.9

* The three ratios are not of true horizons; the C horizon lies much deeper.

† The values given are not horizontal but are for "soil" and "subsoil."

amounts of carbonates tends to increase, the experimental errors become a larger factor in the results reported.

One of the probable influences which produce the decrease in the ratio with increase in depth is the difference in composition of roots of plants as compared with their stems, branches, and leaves. Little definite information on this point is available. Indeed, there is a somewhat remarkable lack of information about the composition of roots. Some data on fleshy roots, such as beets and turnips, indicate a wider carbon-nitrogen ratio than for their leaves, but these are not soil-forming types of vegetation. Unpublished data of this bureau indicate that certain shrubby plants have a lower carbon-nitrogen ratio for their roots than have their tops. For the bulk of soil-forming vegetation such as grasses, cereals, weeds, and trees, no information is at hand. Since it seems probable that a large portion, at least, of the organic matter of the lower portion of the soil is formed there, it is possible that a lowered ratio of the roots is in part responsible.

A more probable influence in some cases and of one greater magnitude is the presence in the upper portions of the soil of charcoal derived from fires which incompletely consume the surface vegetation. More will be said of this in connection with the group distribution.

A third influence which undoubtedly has a large bearing upon the result is a difference in the character of the microbiological processes at and near the soil surface and at lower depths. The writers have no special information on this subject, but it would seem reasonable to assume that the processes of decay taking place at the surface and in the upper portion of the soil profile would result in different residual materials from those occurring under widely different conditions at lower levels.

In any case it appears that nitrogenous materials suffer less complete decomposition or, at least, less rapid conversion to soluble or gaseous forms than do carbohydrate residues. It is pointed out by Salter (24) that organic materials contributing largely to soil organic matter have very large carbon-nitrogen ratios and in the soil these tend to decrease toward smaller values. Thom and Humfeld (27) have shown that the number of microorganisms at the surface of soil roots is vastly greater than in the adjacent soil. This doubtless means that bacteria are utilizing high ratio material as an energy source and are producing carbon-dioxide while at the same time they build up compounds of higher nitrogen content which form bacterial remains. These bacterial remains probably form the larger fraction of soil organic matter. Surface, aerobic organisms may leave different residues than subsurface, anaerobic organisms.

Further, it may be assumed that, even as in the case of the inorganic material, translocation of organic material may occur in the soil. To what extent this occurs is wholly a matter of conjecture except in the case of the podzols, where it is clearly evident that there is large accumulation of organic matter in the B horizon. It seems probable that soluble organic matter from the surface may be precipitated at lower levels as a result of change of pH values and increased base content and this soluble material may be more highly nitrogenous than the original material from which it is separated. This statement is in harmony with the recent work of Joffe (12) on lysimeter extracts through different horizons. Also, it seems reasonable to assume that fractionation of suspended material may occur by the same processes which fractionate and translocate inorganic material; viz., suspension in colloidal form and precipitation and filtration at lower levels. In any case, the result of these or other active influences seems to be a narrowing of the carbon-nitrogen ratio with increasing depth. A study of this relation for the profiles of a given soil series, particularly with reference to colloids, would seem likely to be a fruitful topic.

When we turn to the variations of the carbon-nitrogen ratio among the great soil groups we may expect the same influences which affect the ratio with depth to be operative to a very great extent. Other considerations, however, also enter the problem. The sources of the organic matter are widely different.

In a general way we may say that the chernozem soils considered in table 1 are developed under short grass cover. Those of table 2 are high grass prairie soils Those of table 3 are developed under pine forest cover; those of table 4, under deciduous forest cover; and those of table 5, under deciduous cover and high temperature. It is shown by Salter (24) in the paper previously cited that there is a wide divergence between the carbon-nitrogen ratios of many plants contributing to soil organic matter and, although the short grasses, high prairie grasses, pine needles, and deciduous leaves are not included, there are undoubtedly wide differences. These differences should have an effect even though the trend be *toward* though not *to* a common line.

Again, the great group soils are developed under very different conditions of humidity and temperature and these conditions ought to be expected to result not only in decomposition to varying degrees but because of the differing active organisms should be expected to produce different products. The writers are not aware to what extent the microbiological population of the different soil groups is variable, but it is not a wild assumption if we expect them to be widely different.

A consequence of the different types of vegetation is the difference in the probable presence of charcoal in the soil. In the dry, short grass country, fires are relatively rare and because of the dryness when they do occur the combustion of the organic matter is more likely to be complete. In the high grass prairies the fires are likely to be more frequent and to leave more unconsumed charcoal of small particle size. In the forested areas the natural forest fires and those carried on in clearing operations may cause large variations in carbon content in local ports. Indeed, two of the profiles given in table 3 are known to be so affected.

An influence of unknown magnitude as affecting the data presented in this paper is the extent to which the decomposition of the plant residues is complete. Surface soils in particular may have practically undecomposed fragments of leaves, pine needles, and straw fragments which raise the carbon-nitrogen ratio, and if the same soil be sampled when or where such fragments are not present, the results obtained would be different. It is believed that this is the chief cause of the differences between the surface soil ratios of the Cecil soils in table 5. This is indicated by the ratio shown by the surface colloid, as compared with the soil from which the colloid was extracted.

The carbon-nitrogen ratio of soils is probably also affected by the texture of the A and B horizons, the presence or absence of claypans and hardpans, the extent of erosion, and other influences which determine where and to what extent the organic residues of organic matter are deposited. It is also probable that the ratio is seriously modified seasonally, not only by reason of seasonal production of nitrates, nitrites, and ammonia and their removal through crop growth and drainage but also as a result of the decay, or its lack, of carbohydrates and related compounds.

In considering the rather striking general relations shown in table 6 it must

not be forgotten that the individual soils in each group, except possibly the chernozem and prairie groups, show very wide variation from the mean, and that nothing is presented in general as indicating the causes of these variations.

Despite all these qualifications, however, the writers believe that the results indicate a definite difference in the general character of the soil organic matter in the different groups, and they propose further study along this line in the hope that as additional data are assembled light may not alone be thrown upon the causes of variation but upon the chemical composition of the product. It would be helpful if soil students, when dealing with profile studies whether of soil or colloid, were to make careful record of both total carbon and total nitrogen content.

SUMMARY

A study is made of the available data on the carbon-nitrogen ratio of soils with reference to their classification in the great soil groups. In each group the ratio decreases with depth, though this decrease in neither uniform nor absolutely general. The mean nitrogen content of the surface soils of the great soil groups is also given.

The variations of the carbon-nitrogen ratio are so wide as to make the determination of nitrogen wholly useless as means of estimation of either carbon or organic matter.

The data indicate a wide variation in the ratio between the great groups and also a highly variable ratio in different soils within each group. The most constant ratio is found in the chernozem group. It is more variable in the prairie group and becomes erratic in the other groups.

The possible and probable factors which determine the magnitude of the ratio are discussed, and the conclusion is reached that the results indicate an essential difference in the organic matter of the different groups. The need of study of this relation, particularly with reference to definite soil series and their colloids, is indicated and cooperation is asked.

REFERENCES

(1) ALEXANDER, L. T., AND BYERS, H. G. 1932 A critical laboratory review of methods of determining organic matter and carbonates in soil. U. S. Dept. Agr. Tech. Bul. 317.

(2) ALWAY, F. J., AND VAIL, C. E. 1912 The relative amounts of nitrogen and humus in some Nebraska soils. *Nebr. Agr. Exp. Sta. Ann. Rpt.* 1912: 145–163.

(3) ANDERSON, M. S., AND BYERS, H. G. 1931 Character of the colloidal materials in the profiles of certain major soil groups. U. S. Dept. Agr. Tech. Bul. 228.

(4) ANDERSON, M. S., AND BYERS, H. G. 1933 Character and behavior of organic soil colloids. U. S. Dept. Agr. Tech. Bul. 377.

(5) BENNETT, H. H., AND ALLISON, R. V. 1928 The Soils of Cuba. Washington, D. C.

(6) BROWN, I. C., AND BYERS, H. G. 1932 The fractionation, composition and hypothetical constitution of certain colloids derived from the great soil groups. U. S. Dept. Agr. Tech. Bul. 319.

(7) BROWN, I. C., RICE, T. D., AND BYERS, H. G. 1933 A study of claypan soils. U. S. Dept. Agr. Tech. Bul. 399.

(8) BROWN, P. E., AND O'NEAL, A. M. 1923 The color of soils in relation to organic matter content. *Iowa Agr. Exp. Sta. Res. Bul.* 75: 275–300.

(9) BYERS, H. G. 1933 The constitution of the inorganic soil colloids. *Rept. 13th Ann. Meeting Amer. Soil Survey Assoc. Bul.* 14: 47–52.

(10) BYERS, H. G., AND ANDERSON, M. S. 1932 The composition of soil colloids in relation to soil classification. *Jour. Phys. Chem.* 36: 348–366.

(11) JENNY, H. 1929 Relation of temperature to the amount of nitrogen in soils. *Soil Sci.* 27: 169–188.

(12) JOFFE, J. S. 1933 Lysimeter studies: III. The movement and translocation of nitrogen and organic constituents in the profile of a podzolic soil. *Soil Sci.* 35: 401–411.

(13) JOFFE, J. S., AND WATSON, C. W. 1933 Soil profile studies: V. Mature podzols. *Soil Sci.* 35: 313–331.

(14) LEHAY, A. 1932 Leaching of mineral matter in some Alberta soils. *Sci. Agr.* 13: 7–15.

(15) LEIGHTY, W. R., AND SHOREY, E. C. 1930 Some carbon-nitrogen relations in soils. *Soil Sci.* 30: 257–266.

(16) LYON, T. L., AND BUCKMAN, H. O. 1929 The Nature and Properties of Soils. New York.

(17) MCKIBBEN, R. R., AND GRAY, P. H. H. 1932 Chemical and microbiological factors in some Quebec soils. *Canad. Jour. Res.* 7: 300–327.

(18) MCLEAN, B. W. 1930 The carbon-nitrogen ratio of soil organic matter. *Jour. Agr. Sci.* 20: 348–354.

(19) MARBUT, C. F. 1927 A scheme for soil classification. *First Internatl. Cong. Soil Sci. Proc. and Papers Comn.* 5, v. 4: 1–31.

(20) MARBUT, C. F. 1933 Soils of the United States. Atlas of American Agriculture, Part 3, Advance Sheets No. 8.

(21) MIDDLETON, H. E., SLATER, C. S., AND BYERS, H. G. 1932 Physical and chemical characteristics of the soils from the erosion stations. U. S. Dept. Agr. Tech. Bul. 316.

(22) ROBINSON, G. W. Soils; Their Origin, Constitution and Classification. London.

(23) ROBINSON, W. O., AND HOLMES, R. S. 1924 The chemical composition of soil colloids. U. S. Dept. Agr. Bul. 1311.

(24) SALTER, F. J. 1931 The carbon-nitrogen ratio in relation to the accumulation of organic matter in soils. *Soil Sci.* 31: 413–430.

(25) SIEVERS, F. J. 1930 Further evidence concerning the significance of nitrogen in soil organic matter relationships. *Jour. Amer. Soc. Agron.* 22: 10–13.

(26) STEWART, ROBERT 1910 Quantitative relationships of carbon, phosphorus and nitrogen in soils. *Ill. Agr. Exp. Sta. Bul.* 145: 91–127.

(27) THOM, CHARLES, AND HUMFELD, HARRY 1932 Notes on the association of micro-organisms and roots. *Soil Sci.* 34: 29–36.

A RAPID METHOD FOR THE DETERMINATION OF TOTAL NITROGEN IN SOIL[1]

E. M. EMMERT

Kentucky Agricultural Experiment Station

Received for publication August 30, 1933

In previous papers (1, 2) a method was described for determining total nitrogen by oxidizing with sodium chlorate and sulfuric acid, distilling, and determining nitric acid in the distillate by the phenoldisulfonic-acid method. This procedure, though more rapid than the standard Kjeldahl method, requires considerable time and equipment, and the technic is rather exacting. Recent work has shown that by regulating conditions properly, distillation can be dispensed with. The nitrogen in the soil was oxidized to nitrate at 100°C. in acid solution, and the solution with an excess of chlorate present was neutralized with sodium hydroxide. The precipitated hydroxides and silica were filtered off and an aliquot of the filtrate was treated with fuming sulfuric acid to decompose and expell the excess chloric acid and to make the action of the phenoldisulfonic acid more effective by causing a high acid concentration. The phenoldisulfonic acid was then added and total nitrogen calculated from the nitrate nitrogen found. The following procedure was found satisfactory and can be completed in 10 to 15 minutes, the technic and apparatus being very simple.

PROCEDURE

To 0.2 to 1.0 gm. of finely ground dry soil (the sample should contain at least 0.5 mgm. of N) in a dry 20 x 150 mm. test tube, add by means of a pipette exactly 1 cc. of a 50 per cent solution of sodium chlorate, placing the solution in the bottom of the tube without touching the sides. Samples high in organic matter but low in nitrogen may require 2 cc. of the chlorate solution. Add exactly 3 cc. of a 50 per cent by volume solution of sulfuric acid. Shake the tube and heat the upper part of the solution while shaking until the reaction starts, but not long enough to boil off water. Put the tube into boiling water in such a manner that the water comes to the top of the solution in the tube. Keep in the boiling water until the soil is completely oxidized (usually about 5 minutes, although a longer time will do no harm). The oxidation is complete when a clear yellow or brownish solution is present with a white to brownish silica residue which settles readily. Care should be taken that appreciable

[1] The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published with permission of the director.

overcome the loss due to chlorides which is experienced with dry salts. Evidently, nitrosyl chloride is not formed in the presence of water and as long as the acid is not diluted too much the reaction between nitrate and the phenoldisulfonic acid is complete.

On cooling, sodium sulfate may crystallize out of the neutralized yellow solution, especially if the volume is kept small. For accurate work it is best not to pour or filter off these crystals, since the hydration of the crystallized salts tends to concentrate the solution and cause high results. It is best to warm the solutions a little or keep them warm enough to prevent crystallization. In fact, the most accurate colorimetric readings are obtained immediately after dilution to the final volume, before the solution has a chance to change temperature very much and cause slight volume changes and crystallize out any salts. The same applies to the solution filtered off the soils after oxidation and neutralization. Crystals forming in the solution before the aliquot is taken may cause slight error. The solution should be kept warm enough to prevent crystallization but of course not heated so that an appreciable loss of water results.

REFERENCES

(1) EMMERT, E. M. 1929 The chlorate method for the determination of nitrate nitrogen, total nitrogen and other elements in soils and plant tissues. *Jour. Assoc. Off. Agr. Chem.* 12: 240–247.

(2) EMMERT, E. M. 1930 Procedure for determining total nitrogen by conversion to nitric acid. *Jour. Assoc. Off. Agr. Chem.* 13: 146–147.

(3) Standard Methods for the Examination of Water and Sewage, ed. 6, p. 20. American Public Health Assn., New York, 1925.

NEWER ASPECTS OF NITRIFICATION: I

G. GOPALA RAO

University College of Science, Andhra University, Waltair, India

Received for publication August 30, 1933

It is well known that ammonia, ammonium salts, and other complex nitrogenous compounds are slowly oxidized in the soil to nitrite and nitrate. This oxidation of ammonia to nitrite and nitrate is technically known as "nitrification" and is one of the most important of soil chemical processes from the point of soil fertility. It is now believed almost universally that this nitrification is in the main due to the action of nitrifying bacteria. Pasteur (12) was the first to suggest that the oxidation of ammonia is accomplished by the agency of microörganisms. This view was definitely confirmed by Schlosing and Muntz (15) and by Warington (17). After many investigators had vainly endeavored to obtain nitrifying bacteria of the soil in pure culture, Winogradsky (18) was successful. The researches of Warington and Winogradsky led to the view that nitrification was really due to the joint action of two organisms: one converts ammonia and its salts to nitrites and the other converts nitrites to nitrates but has no effect on ammonium salts.

In view of the foregoing, it is of interest to question whether the nitrification in soils is entirely due to the action of bacteria or whether it is partly due to some other agency. Gopala Rao and Dhar (6) have recently suggested that nitrification in soils must be in part purely photochemical in nature, taking place at the surface of the soil under the influence of sunlight. This view has been based on their experiments on the photochemical oxidation of ammonia and its salts in sunlight in the presence of various photosensitizers like titanium dioxide, aluminum trioxide, zinc oxide, and cadmium oxide. They have found that ammonia is oxidized to nitrite under these conditions. The present paper is devoted to the discussion of the considerable direct and indirect evidence which the author has been able to collect in favor of the photochemical view of nitrification in the soil. He has found that not only ammonium salts but also aqueous solutions of urea, acetamide, hydroxylamine hydrochloride, hydrazine hydrochloride, ethylamine, methylamine, etc. are oxidized to nitrite in sunlight under suitable conditions. It has been found that urea, acetamide, and some other substances are first converted into ammonia under the action of light, and then this ammonia appears to be oxidized to nitrite.

EXPERIMENTAL

It has been observed by several workers that ammonia is slowly oxidized in aqueous solution to nitrite when exposed to the light from a quartz mercury

vapor lamp. It has now been found that this oxidation takes place very slowly in sunlight as well. The present writer has further found that the rate of photochemical oxidation of ammonia in sunlight is increased considerably in the presence of various photocatalysts like zinc oxide, cadmium oxide, titamium dioxide, and aluminum trioxide. The ignited oxides are generally more active photocatalysts than the freshly precipitated oxides. In the presence of the basic oxides like zinc oxide, ammonium salts are also oxidized; if titania is used as a photocatalyst, only ammonia and ammonium carbonate are oxidized in aqueous solution; solutions of ammonium sulfate, chloride, etc., however, can be oxidized, if magnesium or calcium carbonate is added together with titania.

As it is very essential for the present thesis to show that the oxidation of ammonia can take place photochemically in the absence of any bacteria, rigorous precautions were taken to prevent the contamination of the reacting system by bacteria. The apparatus used for this purpose is shown in figure 1. *A* is an Erlenmeyer flask of about 2 liters capacity, fitted with a three-hole stopper. Each of the outer holes carries a piece of glass tubing bent at right angles—*B* reaching to the bottom of the vessel, and *C* just passing through the stopper. Through the middle hole passes an ordinary three-way tap, and of the three limbs *D*, *E*, and *F*, *D* reaches almost the bottom of the bottle. On *E* is blown a bulb *H* of about 20 cc. capacity and *F* is bent at right angles. *B*, *C*, and *E* are plugged with cotton wool. Thus by means of the tap, *E* can be put in communication with *D* and a sample drawn into the bulb *H*, then by suitably manipulating the tap, *D* can be cut off from *E* and the sample run off through the tube *F* into any convenient receptacle. The side tubes *B* and *C* provide a means by which the nitrifying solution can be thoroughly aerated. By attaching *B* to a series of wash bottles containing, in order, sulfuric acid, caustic soda solution, sterile water, and cotton wool it became possible to pass air (free from any nitrous gases) through the experimental solution under aseptic conditions. By this means, then, on the withdrawal of a sample, all air entering the bottle was filtered through cotton wool and the sample remained under strictly aseptic conditions until it was actually expelled from the apparatus.

Before the experiment was begun all parts of the apparatus were sterilized by steam. All solutions were made up with sterile water. In order to check the asepticity of the solutions, one solution identical in all respects with the sample exposed to light was kept in the dark. The entire absence of any reaction in the dark shows the freedom from contamination with any nitrifying bacteria. These experiments have convinced the writer that oxidation of ammonia to nitrite takes place in the entire absence of bacteria under the influence of sunlight and photocatalysts.

Methods of analysis

Modified iodometric method. For the estimation of small quantities of nitrites the permanganate method of titration is neither accurate nor delicate.

After a good number of trials the author has found that the following modification of the iodometric method of Warburg is very suitable for the estimation of minute quantities of nitrites:

To about 20 cc. of the solution were added, first, 4 gm. of sodium bicarbonate, then 5 cc. of 5 per cent potassium iodide and starch indicator solutions. A rapid stream of carbon dioxide was passed through the mixture for about 5 minutes to drive out all dissolved oxygen.

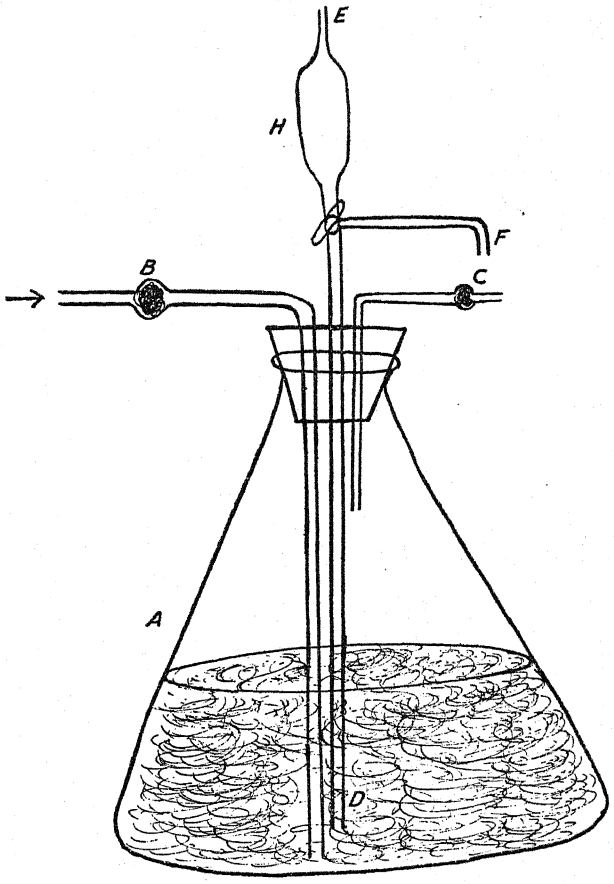


FIG. 1. APPARATUS DESIGNED TO SHOW THE PHOTOCHEMICAL OXIDATION OF AMMONIA IN THE ABSENCE OF BACTERIA

The solution was then acidified with 10 cc. of 5 *N* oxygen-free sulfuric acid, and the liberated iodine was titrated with 0.002 *N* sodium thiosulfate. The sodium thiosulfate solution was standardized against Kahlbaum's analytical potassium dichromate. This method of estimation of nitrite was checked against a standard solution of sodium nitrite prepared from pure silver nitrite.

The essential reaction in the iodometric estimation of nitrite is $2HNO_2 + 2HI = 2H_2O + I_2 + 2NO$. The liberated nitric oxide tends to be oxidized to

nitrogen peroxide, which liberates more iodine from acidified potassium iodide. Hence the amount of liberated iodine will be more than that corresponding to the equation, and the results for nitrite will be rather too high. In order to prevent the results being vitiated by this factor, two conditions must be fulfilled:

First, there should be no dissolved oxygen in the reaction mixture. This condition is obtained by passing through the solution carbon dioxide, which drives out all the oxygen and keeps the solution in an atmosphere of carbon dioxide.

Secondly, the nitric oxide should be driven out of the system as soon as it is liberated. This is accomplished by adding to the initial solution some sodium bicarbonate, which on subsequent acidification liberates large quantities of carbon dioxide simultaneously with the liberation of nitric oxide, which will therefore be driven out.

With these two conditions satisfied the amount of iodine liberated corresponds exactly to that given by the equation. The extreme sensitiveness and accuracy of this method of estimation of nitrites give it an advantage over other methods.

Colorimetric method. When the quantities of nitrites to be estimated are extremely small, however, even this method cannot be used, and resort must be made to the colorimetric methods. We know that nitrite gives an intense pink color with a solution of α-naphthylamine, sulfanilic acid, and acetic acid (Griess-Ilosvay Reaction). For the quantitative application of this method the following procedure was adopted:

Three solutions were made up and stocked.

Nitrite reagent. 0.5 gm. of sulfanilic acid was dissolved in 150 cc. of dilute acetic acid. To this was added a solution made by boiling 0.1 gr. of α-naphthylamine hydrochloride with a little water and adding enough dilute acetic acid to bring the volume up to 300 cc. This reagent should be protected from contact with air and replaced if it develops a noticeable pink color.

Glacial acetic acid.

Standard sodium nitrite solution. This was prepared from pure silver nitrite. Concentrated potassium nitrite solution was treated with silver nitrate, and the precipitate of silver nitrite obtained was filtered and washed with cold distilled water. It was then dissolved in a little hot water and rapidly cooled. The resulting crystals were filtered by suction, washed with cold water, and dried in a desiccator in the dark over calcium chloride. Then 0.1539 gm. of the pure dry silver nitrite was weighed out, dissolved in hot water, and treated with a slight excess of pure sodium chloride solution to precipitate the silver. The mixture was cooled, the precipitated silver chloride filtered off, and the filtrate diluted to 1,000 cc. This gives a standard 0.001 *N* sodium nitrite solution. As a standard for colorimetric estimations, it is diluted ten times.

About 5 cc. of the solution in which nitrite is to be estimated is run into a beaker. Then 2 cc. of the nitrite reagent and 2 cc. of glacial acetic acid are added, and the solution is made up to 40 cc. by the addition of distilled water. At the same time, to another beaker are added 2 cc. of 0.0001 *N* nitrite solution and the same quantities of nitrite reagent and acetic acid, and the solution is diluted to 40 cc. with distilled water. The contents of the two beakers are well stirred and are kept for about one-half hour until the color develops fully, after which 20 cc. of each solution is transferred into the cylinders of a Dubosq colorimeter and the amount of nitrite is estimated in the usual manner.

This method gives very considerable accuracy with higher dilutions of nitrites, but when the concentration of "nitrous" nitrogen rises above two or three parts per hundred thousand the matching of the colors becomes difficult and the accuracy of the determinations is questionable. In such cases the solution is diluted many times and the dilute solution utilized in the colorimetric determination.

Modified Devarda method. When the quantity of nitrite formed is appreciable, the estimation is best done by Allen's modification of the Devarda method. The method is based upon the quantitative reduction of nitrates and nitrites to ammonia in an alkaline solution by an alloy consisting of 45 parts of aluminium, 50 parts of copper, and 5 parts of zinc. The ammonia evolved is distilled into standard sulfuric acid and thus estimated.

EXPERIMENTAL RESULTS

Oxidation of ammonia and its salts in ultraviolet light

I have observed that ammonia is slowly oxidized in aqueous solution to nitrite, when exposed to the light from a quartz mercury vapor lamp or a copper arc and more slowly in sunlight. The nitrite can easily be detected by the color reaction given by α-naphthylamine and sulfanilic acid. Ammonium salts are also oxidized to nitrites, the reaction being slower in the case of the sulfate and chloride than in that of the carbonate.

Quantitative work in monochromatic light is in progress.

Oxidation of ammonia and its salts in sunlight in the presence of photosensitizers

We have found that the rate of the photochemical oxidation of aqueous solutions of ammonia and its salts is considerably increased in the presence of small quantities of photosensitizers like ignited titanium dioxide, zinc oxide, cadmium oxide, aluminum oxide, and silica. There is no reaction in the dark in any of these cases. Most soils contain titanium dioxide to the extent of 0.3–0.6 per cent, as shown by Geilman (5). Hence experiments done with titanium dioxide as a photosensitizer would be more pertinent from the point of soil nitrification.

To determine the effect of varying amounts of TiO_2 on the oxidation of aqueous solutions of ammonia, 100 cc. of 0.8 *N* ammonia solutions were exposed to sunlight for 20 hours in several glass bottles with varying amounts of titania. Air freed from nitrous fumes was passed through each bottle slowly at the same rate. In an ammoniacal solution titania is peptized, giving a colloidal solution which passes through the filter paper. Hence after exposure the titania was coagulated by the addition of a little barium chloride solution, filtered, and the clear filtrate made up to 100 cc. Of this liquid 20-cc. portions were taken, and the nitrite content was estimated by the iodometric method outlined in the foregoing. The results are given in table 1.

Experiments in which the same amount of TiO_2 was used with varying concentrations of ammonia gave the results shown in table 2.

TABLE 1

Effect of Varying Amounts of TiO_2 on the Oxidation of Aqueous Solutions of Ammonia

Exposure 20 hours, 100 cc. 0.8 *N* ammonia solution

AMOUNT OF TiO_2	NITRITE NITROGEN PER LITER
gm.	*mgm.*
0.006250	3.149
0.012500	6.509
0.025000	10.080
0.0500000	14.000
0.100000	18.200
0.200000	21.840
0.300000	24.600
0.400000	24.580
0.500000	24.600

TABLE 2

Effect of Varying Concentrations of Ammonia

Exposure to sunlight 20 hours, 0.1 gm. TiO_2 + 100 cc. of ammonia solution

CONCENTRATION OF AMMONIA	NITRITE NITROGEN FORMED PER LITER
	mgm.
0.32 *M*	15.530
0.16 *M*	14.700
0.08 *M*	11.270
0.04 *M*	8.399
0.02 *M*	6.789
0.01 *M*	5.040

TABLE 3

Influence of foreign substances

Exposure to sunlight 12 hours, 100 cc. of 0.8 *N* ammonia solution + 0.1 gm. TiO_2

SUBSTANCES ADDED	NITRITE NITROGEN FORMED PER LITER
	mgm.
nil	10.080
0.2 *N* sodium chloride	4.200
0.2 *N* potassium oxalate	4.200
0.2 *N* sodium benzoate	1.120
0.01 *N* sodium thiocyanate	3.080
0.5 per cent quinine sulfate	0.280

Table 3 shows the influence of foreign substances. It is interesting to note that even the addition of a neutral inorganic substance like sodium chloride

retards the velocity of oxidation of ammonia to nitrite. The mechanism of this inhibitory action will form an interesting subject for further research. The author suggests the following tentative explanation. It appears that the oxidation of ammonia takes place at the surface of the colloidal particles of titania. This is supported by the fact that ammonia is considerably adsorbed by titania. Sodium chloride coagulates the colloidal titania, causing an agglomeration of the particles, thus decreasing the available surface. Of all the substances so far studied quinine sulfate is the most active inhibitor of the photochemical oxidation. This result is easily explained by the fact that quinine sulfate is a fluorescent substance that absorbs light of short wavelength (which is responsible for the oxidation of ammonia) and degrades it into light of longer wavelength.

There is very little oxidation of ammonium sulfate in the presence of sunlight and titania, but if a basic substance like $CaCO_3$ is present besides, oxidation takes place readily. An alkaline reaction is essential for nitrite formation. In the absence of basic carbonates, only ammonium carbonate and ammonia are oxidized. In the presence of sodium, magnesium, or calcium carbonate, the sulfate, phosphate, and chloride as well as the other salts of ammonium can nitrify. The presence of a base in the medium is essential as a neutralizing agent to prevent the reaction of the medium becoming too acid as a result of the formation of nitrous and sulfuric acids from the oxidation of the ammonium sulfate.

It is interesting to note that the bacterial and photochemical nitrification processes are very similar in the foregoing aspects. In the following experiments 100 cc. of ammonium sulfate solution was exposed to sunlight for 17 hours, with 0.2 gm. of titania and 1.00 gm. of calcium carbonate. The results recorded in table 4 show that a decrease in concentration of the ammonium salt decreases the rate of formation of nitrite only to a slight extent.

The progress of the reaction of ammonia with varying lengths of exposure is shown in table 6. In this experiment, 500 cc. of 0.8 *N* ammonia solution was exposed to sunlight from day to day with 0.5 gm. of titania. Each day the exposure lasted for 5 hours, from 11 a.m. to 4 p.m. At the end of every 5 hours' exposure, 100-cc. portions of the solution were taken out and the nitrite content was estimated as usual.

Table 7 shows the effects of varying lengths of exposure of ammonium sulfate. For this experiment, 500 cc. of 0.1 *M* ammonium sulfate solution was exposed with 5 gm. of titania and 10 gm. of calcium carbonate. Every day the solution was exposed to sunlight for 5 hours. At the end of every 10 hours' exposure 100-cc. portions of the liquid were withdrawn and the nitrite content was estimated. It will be seen from the results recorded in table 7 that the amount of nitrite formed increases with time of exposure almost in direct proportion.

TABLE 4

Effect of varying the concentration of ammonium sulfate

CONCENTRATION	NITRITE NITROGEN FORMED PER LITER
	mgm.
1.00 *N*	6.299
0.50 *N*	5.948
0.25 *N*	4.899
0.125 *N*	4.200
0.03125 *N*	2.940
0.01562 *N*	2.170
0.0781 *N*	1.288
0.003905 *N*	0.6998

TABLE 5

Effect of varying the amount of titania

Exposure 20 hours, 100 cc. 0.2 *N* $(NH_4)_2SO_4$ + 1.0 gm. of $CaCO_3$

AMOUNT OF TITANIA	NITRITE NITROGEN FORMED PER LITER
gm.	*mgm.*
0.1	4.060
0.2	5.249
0.3	5.740
0.4	5.740

TABLE 6

Effect of varying lengths of exposure on ammonia

TIME OF EXPOSURE	NITRITE NITROGEN FORMED PER LITER
hours	*mgm.*
5	6.580
10	12.880
15	19.730
20	26.310
25	33.040

TABLE 7

Effect of varying lengths of exposure on ammonium sulfate

TIME OF EXPOSURE	NITRITE NITROGEN FORMED PER LITER
hours	*mgm.*
10	2.920
20	5.780
30	8.760
40	11.340
50	14.560

Comparative rates of bacterial and photochemical nitrification

The quantities of nitric nitrogen formed in the photosensitized oxidation of ammonium salts in the presence of titania and sunlight compare favorably with those obtained in the bacterial nitrification. Very recently Cutler and Mukerji (4) isolated new strains of nitrifying organisms other than Nitrosomonas. In one of their best experiments these workers obtained, with a solution of ammonium sulfate containing 0.02 gm. nitrogen per 100 cc., 0.25 mgm. of nitrite nitrogen per liter in 144 hours; whereas in the photochemical nitrification the author has obtained (table 4), with a solution containing 0.022 gm. nitrogen per 100 cc., 2.170 mgm. of nitrite nitrogen per liter in only 17 hours; in 144 hours the yield of nitrite nitrogen would have been *18.39* mgm. Under the same conditions, therefore, the photochemical process yields about 74 times more nitrite nitrogen than the bacteria isolated by Cutler and Mukerji. If we take the yield of nitrite nitrogen in a quartz vessel, it would be 200 times more.

It will be seen from the following results that the rate of photonitrification is approximately three times faster in the quartz vessel than that in the glass vessel.

	mgm. nitrite nitrogen formed per liter
100 cc. of 0.8 *N* ammonia solution exposed for 20 hours in a glass flask with 0.1 gm. of titania	18.200
100 cc. of 0.8 *N* ammonia solution exposed for 20 hours in quartz flask with 0.1 gm. of titania	52.190

To determine the effect of alumina and humic acid as catalysts of photonitrification, 100 cc. of solutions of ammonia and various ammonium salts were exposed to sunlight in glass vessels with 0.2 gm. of aluminum trioxide (Merck's) for 60 hours. The amount of nitrite formed was estimated colorimetrically, with the following results:

Substance	*mgm. nitrite nitrogen formed per liter of solution*
Ammonia 0.2 *N*	0.848
Ammonium chloride 0.2 *N*	0.747
Ammonium sulfate 0.2 *N*	0.750
Ammonium lactate 0.2 *N*	Nil
Ammonium acetate	0.090
Ammonium malonate	Nil

It was found that humic acid obtained from the soil also acts as a photocatalyst for the oxidation of ammonia to nitrite. In one case 100 cc. of 0.2 *N* ammonia solution was exposed to sunlight for 60 hours in a glass vessel with 0.1 gm. of humic acid under strictly aseptic conditions. The amount of nitrite nitrogen obtained by photo-oxidation was 0.896 mgm. per liter of solution. A control kept in the dark gave no test for nitrite. Further work is in progress on the rôle of humic acid in soil nitrification from the photochemical point of view.

Oxidation of ammonia in sunlight in the presence of sterilized soil

The final proof that nitrification in the soil is partly photochemical comes from experiments with sterilized soil as a photocatalyst. Ordinary garden soil was heated to 200°C. for several hours so as to ensure the complete destruction of all bacteria. Then it was washed several times with hot water to remove any nitrite and nitrate originally present and stirred up with an aqueous solution of ammonia. This was then exposed to sunlight in a glass or quartz vessel under aseptic conditions. Oxidation of ammonia to nitrite was always noticed. Quantitative experiments along this line are in progress.

Oxidation of urea and other nitrogenous compounds

It has also been found that various amines, amides, and amino acids are oxidized to nitrite in the presence of sunlight. The conversion of these compounds into ammonia appears to be a first stage in their final oxidation to nitrite. Aliphatic nitrogen compounds are more easily converted to ammonia than are aromatic compounds. Urea and acetamide are more readily decomposed than is benzamide, and ethylamine and methylamine are more readily decomposed than is aniline or diphenylamine. Urea hydrolyses to ammonia readily, but thiourea does not.

Amino-acids, e.g., glycine, alanine, aspartic acid, and glutamic acid, are gradually decomposed on exposure to sunlight into the corresponding aldehyde, ammonia, and carbon dioxide. In the case of glycine, formaldehyde, ammonia, and carbon dioxide are formed:

$$CH_2NH_2COOH + (0) = H\cdot CHO + NH_3 + CO_2$$

The ammonia thus formed is slowly oxidized to nitrite. Detailed results will be published in another paper.

DISCUSSION OF RESULTS

The experiments on the photochemical nitrification of ammonia and its salts, and many other classes of nitrogenous compounds like amides, amines, and amino-acids are remarkably interesting and point to far reaching conclusions with regard to the problem of nitrification in the soil. Hitherto it was believed that this oxidation is entirely due to bacteria, but the following facts cannot be made to fit in with the bacterial explanation:

Omeliansky and Meyerhof (10a, 11a) showed that for the bacterial nitrification process a higher concentration of ammonia or nitrite is harmful (the optimum concentration is about 0.05 per cent with a second optimum at 0.1 per cent; over 0.3 per cent interferes with the process). But in certain localities, the so-called niter spots, a high concentration of nitrite and nitrate, varying from 5–20 per cent of the bulk of the soil, has been noticed. The biological explanation cannot be entirely sufficient for the accumulation of the nitrates, as the high concentration of nitrite and nitrate should inhibit the action of the nitrifying organisms.

Several workers [Green (7), Lemmermann and Wichers (10), Jensen (9), Smith (16), and Batham and Nigam (1)] have observed a periodic variation of the nitric nitrogen con-

tent of soils. They made the important observation that the nitrifying capacity of the soil is maximum in the summer months and minimum in the winter. Experiments made in the laboratory and in the field have yielded similar results.

The curves given in Batham and Nigam's paper show that the trend of nitrate content of soils is downward from summer to winter and upward from winter to summer. The maximum solar activity occurs in the northern hemisphere in June and July and the minimum in the month of December. Accordingly the curve shows the maximum nitrate content in June–July and the minimum in December. Further it will also be seen from Batham's paper that when the average figures for the nitric nitrogen content of the autumn and spring seasons of the northern hemisphere are taken into consideration, it is found they are nearly the same, and both of them are greater than the winter figure and less than the summer one. Because the two seasons are equinoctial, the earth receives nearly the same measure of solar energy, which is greater than that received during the winter and less than that received during the summer. It will be thus seen that there is a close correlation between the solar activity and the nitric nitrogen content of the soil.

Again the northern and southern hemispheres are reciprocal in their seasons and in the lengths of their days and nights. In the southern hemisphere the solar activity is at its maximum in December and January, hence the nitric nitrogen content of the soils of the southern hemisphere must also be greatest at this time of the year. Batham and Nigam (1) have collected data of other workers to show that the nitrate content of soils of the southern hemisphere is greatest in December–January and is at its minimum in the months of June–July. Thus, as the two hemispheres are reciprocal in their seasons, they are also reciprocal in the manner of variation of the nitrate content of their soils during the different seasons of the year. More recently Prescott and Piper (13) have shown, working in South Australia, that nitrate accumulation was maximum in the months of November and December, and minimum in the months of June and July. It must be remembered that in Australia the maximum solar activity occurs in November and December, the hottest part of the year. It appears to be generally established, therefore, that nitrification is maximum in the summer and minimum in the winter.

This fact has not yet received any suitable explanation. It cannot be that sunlight stimulates the action of nitrifying bacteria, for Warington showed, several years ago, that sunlight inhibits the action of nitrifying bacteria. Besides, the high temperature reached by the soil (as high as 50° in tropical countries) is inimical to bacterial action. Hence nitrate accumulation due to bacteria should be minimum in the summer months. On the contrary it is at its maximum. This shows that there must be some other agency which also brings about nitrification, and this agency, unlike bacteria, must be favorably influenced by sunlight. Now the author has shown conclusively that the nitrification of ammonium salts and the complex nitrogenous compounds can take place in the complete absence of bacteria, if only sunlight

and photocatalysts like titania and alumina be present. Nitrification, therefore, appears to take place normally, at least to a certain extent, in the soil by the photochemical action of sunlight and soil photocatalysts like titania and alumina. Since the solar light energy is available in greater amounts in summer than in winter, the accumulation of nitrates is greatest in summer and least in winter.

It might be suggested that the periodic variation of the nitrate content of soils is due to the variation in the amount of rainfall. In the summer months there is less rainfall, and hence not much nitrate will be washed down into the lower layers of the soil. In winter months it might be that more nitrate is washed down by the greater amount of rainfall. This explanation cannot be correct in view of the following considerations. Prescott and Piper (13) have studied the distribution of the nitrate and nitrite in the various soil levels. The bulk of the nitrate and nitrite is located in the surface mulch as will be seen from table 8.

The effect of the rain is to wash down the nitrate from the surface and to redistribute this in the top 18 inches. In order to eliminate the disturbing

TABLE 8

Distribution of nitrate at different depths

DEPTH	NITRATE NITROGEN (P.P.M. OF DRY SOIL)	
	Autumn 1926	Autumn 1929
inches		
0–3½	72	73
3½–9	7	10
9–18	6	4
18–27	..	..

influence of the rain, Prescott and Piper have studied seasonal variation of the total nitrate and nitrite in the top 18 inches of the soil of various field plots. Their results, which take into account the nitrate washed down by the rain, show graphically that the nitrate nitrogen content is at its maximum in November–December (the summer months in Australia) and at its minimum in June–July (the winter months).

Nitric nitrogen also occurs in the atmosphere, as the oxides, N_2O_3 and N_2O_5, or as ammonium nitrite and nitrate. These are washed down to the earth by the rain. What is the source of this nitric nitrogen? It has been thought that oxides of nitrogen owe their origin to thunderstorms in the upper air, where, as a result the electric discharges taking place, nitrogen and oxygen combine to form N_2O_3 and N_2O_5. But be that as it may, thunderstorms do not occur often: they are the exception rather than the rule. Now if N_2O_3 and N_2O_5 are ascribed to thunderstorms, they must be washed down by the rain that follows and should be practically absent from the atmosphere on ordinary days. But this does not hold good. Air tested on any day is sure

to contain oxides of nitrogen in quantities which do not differ much from those found on days when there are thunderstorms. The amount of nitric nitrogen present at any given time does not follow the electrical disturbances in the air.

The author suggests the following explanation for the origin of nitrites and nitrates in the atmosphere. It is well known that ammonia occurs to an appreciable extent in the atmosphere, largely as a product of organic decomposition on the earth. The author has succeeded in oxidizing a solution of ammonia to nitrite by exposing it to light from a quartz mercury vapor lamp or from a copper arc. He has also shown that this oxidation of ammonia can also take place slowly in quartz vessels in ordinary sunlight. It is suggested, therefore, that the nitric nitrogen in the atmosphere owes its origin mainly to the photochemical oxidation of its ammonia content under the short-wave ultraviolet portion of sunlight occurring at the higher altitudes. This theory receives support from the following considerations.

As there is a seasonal variation of the intensity of solar energy in any one locality, it follows from the author's views that there should be a corresponding

TABLE 9

Seasonal variation of nitric nitrogen in the atmosphere

SEASON	NITRIC NITROGEN PER LITER OF RAIN
	mgm.
Winter	0.30
Spring	1.00
Summer	2.00
Autumn	1.00

variation in the nitrogen content of the atmosphere. This corollary appears to be borne out by experiment.

Miller (11) points out that several results obtained in various localities show higher amounts of nitrates in the summer than in the winter. Russel and Richards (14), summarizing the results of a long-continued series of analyses, shown that there is a marked difference between summer and winter rainfall and that the winter rain is characterized by low ammonia and nitrate content whereas the summer rain is characterized by high ammonia and nitrate content.

Bineau (2) made observations at Lyons, which are given in table 9.

All these results show that the nitric nitrogen content of the atmosphere is maximum in the summer and minimum in the winter.

Figure 2 shows in one curve the variation of the total radiant energy from month to month, and in the other curve, the variation of the so-called ozone[1]

[1] It is not the ozone but the nitric nitrogen, for recent work has shown that no ozone is present in the lower air, and the test employed for estimation of ozone is given readily by oxides of nitrogen.

but really the variation of the nitric nitrogen content of the atmosphere from month to month. It is interesting to note how one curve follows the other. From winter to summer the amount of nitrite is on the rise, while from summer to winter it is on the decline, corresponding to changes in the intensity of sunlight.

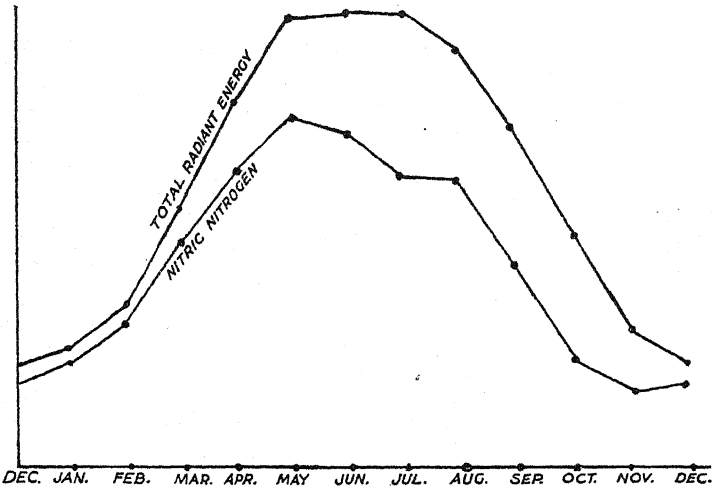


FIG. 2. MONTHLY VARIATIONS OF THE TOTAL RADIANT ENERGY OF THE SUN AND THE NITRIC NITROGEN OF THE ATMOSPHERE

Curves drawn from results of the Radcliffe Observatory, Oxford, vol. 51, p. 214

TABLE 10

*Ammoniacal and nitric nitrogen brought down by rain in various localities**

Data in pounds per acre per annum

LOCALITY	NITRIC NITROGEN	AMMONIACAL NITROGEN	NITRIC N / AMMONIACAL NITROGEN
British Guiana	1.886	1.006	1.874
Barbados	2.443	1.009	2.322
Rothamsted	1.130	2.710	0.419
Kansas	1.060	2.630	0.403
Iceland	0.263	0.802	0.327

* This table is taken from Mellor's comprehensive *Treatise on Inorganic and Theoretical Chemistry*, vol. 8, p. 13.

Hayhurst and Pring (8) find that the proportion of nitric nitrogen is greater at high altitudes than at low altitudes. The ratio of the oxides of nitrogen in the upper air to that in the lower atmosphere was found to be 2.23:1 at 8,500 feet elevation and 1.76:1 at 2,600 feet elevation. This observation is readily explainable on the present photochemical theory, as the proportion of ultraviolet radiation is greater at high than at low altitudes.

As in the tropical countries the length of the day and the intensity of the sun is much greater than in temperate climates, it will be expected that the proportion of nitric nitrogen in the rain of tropical countries will be much higher than that of the rain of temperate climates.

Clarke (3) has compiled the data in table 10 showing the amount of ammoniacal and nitric nitrogen brought down by the rain annually in various localities. The table shows that the ratio of nitric to ammoniacal nitrogen is greater in tropical countries than in the temperate and frigid zones. It will be seen, therefore, that the nitric nitrogen is usually in excess of ammoniacal nitrogen in the rain of tropical countries, but the converse is true of temperate and frigid zones.

SUMMARY

The author has adduced considerable evidence, experimental and otherwise, to show that nitrification in the soil is also partly due to the photochemical action of sunlight. This theory receives added support from the evidence collected to show that the nitrification in the atmosphere is mostly due to the photochemical action of the short-wave ultraviolet portion of sunlight. The author's experiments show that sunlight plays a prominent rôle in the chemistry of soil processes. This important factor has been long overlooked; the author hopes that a clear recognition of this factor will lead to a fundamental modification of our views regarding the mechanism of various material transformations occurring in the soil.

The slow oxidation of ammonia in aqueous solution to nitrite has been shown to take place in transparent silica vessels under the action of the light from a quartz mercury vapor lamp, copper arc, or more slowly in sunlight.

It has also been found that the rate of the oxidation of ammonia in sunlight is considerably increased in the presence of small quantities (as low as 0.1 per cent) of photocatalysts like heated titanium dioxide, aluminum oxide, and zinc oxide. In the presence of these photosensitizers the oxidation also occurs in glass vessels. Ammonium salts can also be thus nitrified, if a basic substance like calcium carbonate is present in the system. Sterilized soil also accelerates the oxidation of ammonia solutions in sunlight.

The oxidation of various complex nitrogenous compounds has also been brought about in sunlight in the presence of the photocatalysts mentioned. Acid amides like acetamide, propionamide, carbamide, or urea are first hydrolyzed photochemically, giving ammonia: and this ammonia is then oxidized to nitrite. Amino acids like glycine, alanine, amino, and succinic acid are first decomposed to ammonia, carbon dioxide, and the corresponding aldehyde. Amines are also oxidized to nitrite.

These experimental results show that nitrification in the soil is at least partly photochemical, taking place without the agency of bacteria under the action of sunlight at the surface of various soil photocatalysts like alumina and titania. There is considerable indirect evidence in favor of this view.

Experiments of several agricultural chemists clearly show that the nitrifying capacity of the soil is maximum in the summer months and minimum in the winter months. This seasonal variation of the nitrate and nitrite content of soils can be successfully explained on the basis of the photochemical view now put forward.

Nitrification in the atmosphere also appears to be due to the photochemical action of sunlight. The monthly variation of the nitric nitrogen content of the atmosphere is closely correlated with the variation of the intensity of sunlight from month to month.

A new method developed by the author for the estimation of small quantities of nitrite has been described. The extreme delicacy and rapidity of the method commend its general use.

APPENDIX

On the non-biological oxidation of nitrite to nitrate

The most important stage in the nitrification process is the one leading to the production of nitrite from ammonia. Even the most powerful oxidizing agents, like chromic acid and potassium permanganate, cannot bring about the oxidation of ammonia to nitrite at ordinary temperatures. But the second stage in the nitrification process, namely, the oxidation of nitrite to nitrate, is easily accomplished. Nitrite easily undergoes oxidation to nitrate by atmospheric oxygen in the presence of acids at ordinary temperatures.

According to Gmelin-Kraut (*Handbuch Anorg. Chem.* 1: 1, 27), Berzelius found a direct oxidation of nitrite to nitrate with air. On the other hand, Matignon and Marchal [*Compt. Rend.* 170: 232 (1920)] were unable to show a direct oxidation in neutral medium. Reinders and Vles [*Rec. Trav. Chim. Pays.-Bas.* 44: no. 1 (1925)] have also arrived at the conclusion that there is no perceptible oxidation of nitrite in neutral or alkaline solution. A weak acid solution of nitrite, however, absorbs oxygen readily. The rate of oxidation of nitrite to nitrate increases with increase in the acidity of the solution. In fact the velocity of the reaction depends on the concentration of free nitrous acid in solution.

It is well known that carbon dioxide can liberate nitrous acid from a nitrite solution, which may easily be demonstrated when a stream of this gas passes through. The acidity of the solution then increases considerably (pH from 8.8 to 5.5). It is clear, therefore, that in the presence of dissolved carbon dioxide the nitrite solution no longer remains alkaline or neutral, but becomes acid. Hence a slow oxidation of the nitrite will follow, because the nitrous acid liberated by carbon dioxide yields nitric acid, which again liberates fresh nitrous acid. In this way we can explain at the same time why Berzelius did notice oxidation in air, while Matignon and Marchal, who worked with great care, were unable to demonstrate a direct oxygen reaction.

From what has been said above, it is clear that a slow oxidation of nitrite to nitrate takes place in the presence of air and carbon dioxide. This reaction is important from the point of soil chemistry; indeed Muntz (quoted in Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. 8, section on Biological Fixation of Nitrogen) has shown that nitrites may be oxidized chemically by the joint action of the carbon dioxide and oxygen of the atmosphere. The author has repeated the experiments of Muntz. Twenty cubic centimeters of 0.002 *N* sodium nitrite solution was put into a flask through which a current of pure carbon dioxide and of purified air was bubbled simultaneously for about 8 hours. At the end of this period the amount of nitrite left over was estimated, by the authors' iodometric method. The following are the results:

Volume of 0.002 N nitrite solution taken	*Equivalent amount of 0.002 N hypo solution before treatment*	*Equivalent amount of 0.002 N hypo soluion after passing CO_2 and air*
25.0 cc.	25.0 cc.	20.00 cc. after 8 hrs.
20.0 cc.	20.0 cc.	16.20 cc. after 8 hrs.
20.0 cc.	20.0 cc.	15.70 cc. after 9 hrs.

These experiments confirm the findings of Muntz that nitrite undergoes oxidation to nitrate under the joint action of carbon dioxide and air.

It is clear from these results that the oxidation of nitrite to nitrate can take place without the action of bacteria in the presence of carbon dioxide and air; and very likely this reaction takes place normally in the soil.

REFERENCES

(1) BATHAM, H. N., AND NIGAM, L. S. 1930 Periodicity of the nitrate content of soils. *Soil Sci.* 29: 181–190.

(2) BINEAU, A. 1854 *Ann. Chim. et Phys.* (3) 42: 462.

(3) CLARKE, F. W. 1921 The Data of Geochemistry, p. 52. Washington, D. C.

(4) CUTLER, D. W., AND MUKERJI, B. K. 1931 Nitrite formation by soil bacteria, other than Nitrosomonas. *Proc. Roy. Soc.* [London] B 108: 384–394.

(5) GEILMANN 1920 Über die Verbreitung des Titans in Böden und Pflanzen. *Jour. Landw.* 68: 107–124.

(6) GOPALA RAO, G., AND DHAR, N. R. 1931 Photosensitized oxidation of ammonia and ammonium salts and the problem of nitrification in soils. *Soil Sci.* 31: 379–384.

(7) GREEN, H. H. 1914 Nitrification in soil tests. *Centbl. Bakt.* (II) 41: 577–608.

(8) HAYHURST, W., AND PRING, J. N. 1910 Examination of the atmosphere at various altitudes for oxides of nitrogen and ozone. *Jour. Chem. Soc.* 97: 868–877.

(9) JENSEN, C. A. 1910 Seasonal nitrification as influenced by crops and tillage. U. S. Dept. Agr. Bur. Plant. Indus. Bul. 173.

(10) LEMMERMANN, O., AND WICHERS, L. 1920 Über den periodischen Einfluss der Jahreszeit auf den Verlauf der Nitrifikation. *Centbl. Bakt.* (II) 50: 33.

(10a) MEYERHOF, O. 1917 *Pflüger's Arch. Physiol.* 166: 240.

(11) MILLER, N. H. J. 1915 Soils and fertilizers. *Ann. Rpts. Prog. Chem.* [London] 12: 211–233.

(11a) OMELIANSKY, W. *Centbl. Bakt.* (II) 5: 473 (1900); 9: 163 (1902).

(12) PASTEUR, L. 1862 *Compt. Rend. Acad. Sci.* [Paris] 54: 265–270.

(13) PRESCOTT, J. A., AND PIPER, G. R. 1930 Nitrate fluctuations in a South Australian soil. *Jour. Agr. Sci.* 20: 517–531.

(14) RUSSEL, E. J., AND RICHARDS, E. H. 1919 The amount and composition of rain falling at Rothamsted. *Jour. Agr. Sci.* 9: 309–337.

(15) SCHLOSING, T., AND MUNTZ, A. 1877 *Compt. Rend. Acad. Sci.* [Paris] 84: 401; 85: 1018.

(16) SMITH, J. B. 1928 Distribution of nitrates in three layers of fallow soil. *Soil Sci.* 26: 347–350.

(17) WARINGTON, R. 1878, 1879 *Jour. Chem. Soc.* 33: 44 (1878); 35: 429 (1879).

(18) WINOGRADSKY, S. 1890, 1891 The formation of nitrates in the process of nitrification. *Ann. Inst. Pasteur* 4: 213, 257 (1890); 5: 92, 577 (1891).



LAWS OF SOIL COLLOIDAL BEHAVIOR: XV. IONIC EXCHANGE WITH HYDROXIDES

A. J. PUGH

New Jersey Agricultural Experiment Station

Received for publication August 21, 1933

The contamination of precipitates by adsorption of substances dissolved in the solution from which they separate is a general phenomenon, but the degree to which various precipitates are contaminated varies widely with different precipitates. The general nature of the process is, however, not known, chiefly because of the widely different viewpoint that occurs between most investigators in this field. Mattson (2) in an investigation of soils and synthetic silicates made an important contribution by correlating the adsorption, both anionic and cationic, with the electrokinetic behavior, and the application of this principle has been extended in this work to hydroxides of the various metals.

Hydroxides are a very important group of compounds, from both the theoretical and the commercial standpoints. Alumina is used as a coagulant in the purification of water supplies, but the chief commercial use of hydroxides is as mordants in the dyeing of fabrics. In general a mordant may be defined as any substance that is adsorbed strongly by the cloth and in turn adsorbs the dye strongly. For this purpose chromium, aluminum, iron, tin, and copper have been used for cotton and wool, while titanium is said to be an extremely good mordant for leather.

The main purpose of this investigation, however, was to determine the influence of pH on the adsorption of anions by the various hydroxides. The adsorption of anions has in the past been confined largely to a determination of the influence of concentration on the degree of adsorption, the influence of pH having been neglected. It has been found that the differential effect of concentration can usually be expressed by the Freundlich adsorption isotherm:

$$\frac{y}{m} = KC^{\frac{1}{p}}$$

where $\frac{y}{m}$ = amount adsorbed per unit of colloid, K and p are constants and C is the final concentration.

Such an equation gives an adequate mathematical expression to the facts, but obscures the nature of the process, as no physical interpretation can be given to it. So many factors enter into the phenomenon of adsorption, such

as the age of the colloid, exchange reactions, and solubility effects, that very little, if any, information can be gained by the use of such a formulation.

THE ISOELECTRIC POINT AND ION EXCHANGE

The composition of the micelle in most colloidal complexes is never known with certainty, as the molecules that polymerize with the formation of colloidal aggregates are many, such as silicates, phosphates, and humates of iron and aluminum in the case of soil colloids. Since we are concerned not so much with their composition, but with their capacity to adsorb and exchange ions, the isoelectric point if characterized by the simultaneous determination of pH gives an extremely important point for a comparison of their properties and exchange reactions (2). When the colloids are regarded as amphoteric electrolytes with one large sluggish ion, the isoelectric point occurs at that pH where the cationic and anionic dissociations are equal and at a minimum.

When an electrodialyzed soil is added to a solution of a neutral salt an exchange acidity is almost invariably developed, for with soils their acid dissociation is much stronger than their basic dissociation and their isoelectric point is always below pH 7.0. If treated with a neutral salt the cation of the salt is exchanged for the hydrion of the colloid, and not the anion of the salt with the hydroxyl of the colloid. Mattson and Hester (4), however, found that if a soil was treated with a salt solution, the pH of which had been adjusted below the isoelectric pH of the colloid, then an exchange alkalinity was developed, the hydroxyl ion being replaced by the anion of the salt.

EXPERIMENTAL

Approximately a liter of the normal solutions of the chlorides of the metals was treated with sodium hydroxide solution, until the isoelectric pH of the colloids, as had previously been determined by cataphoresis, was reached.[1] The pH values at which the various hydroxides are isoelectric are given in table 1.

The floc was separated from the mother liquor by filtration but without washing, the colloid suspended in distilled water and analyzed for the oxide. For the determination of exchange neutrality, an aliquot of the sol was mixed with 100 cc. of the several oxalate solutions in 200-cc. flasks, the total volume in each case being made up to 200 cc. The flasks were shaken at frequent intervals during the day, and the floc was allowed to settle overnight. The "pH after" determination was made on the supernatant liquid with the quinhydrone electrode. A like solution diluted with water instead of with the colloid was used to obtain the "pH before" with the hydrogen electrode. The quantity of oxalate adsorbed was obtained by titrating an aliquot of the supernatant liquid with standard permanganate, and taking the difference of the latter value and the original concentration as the quantity adsorbed. By

[1] Mattson, S. and Pugh, A. J. Unpublished data.

the use of sodium oxalate and oxalic acid of the same concentration, the pH could be varied while the oxalate concentration was kept constant.

U.S. DEPT. OF AGRICULTURE LIBRARY.

ANION ADSORPTION

The adsorption of oxalate and the pH are shown graphically for the various hydroxides in figures 1, 2, 3, 4, and 5. For the stannic, ferric, and chromic hydroxides, the quantity of oxalate adsorbed diminishes consistently with increasing pH of the solution, and in almost all cases there is exchange neutrality with solutions the pH of which is below the isoelectric pH of the colloid and exchange acidity above. Regarding the colloids as amphoteric electrolytes with one sluggish ion permits of a fairly easy interpretation, and the effect is identically the same as has previously been found by Mattson (3) with soils.

Mattson, working with a Nipe soil colloid, discovered that the adsorption of NH_4 from a solution of ammonium chloride took place with increasing pH of the solution and a simultaneous increase in the electronegative charge of the particle. With a decrease in the electronegative charge the adsorption of NH_4 diminished and was accompanied by a lowering of the pH of the ammonium chloride. As the colloid became positively charged the adsorption of

TABLE 1

Isoelectric pH of the hydroxides of the metals prepared from the chlorides

	HYDROXIDE				
	Stannic	Titanic	Ferric	Aluminum	Chronium
pH.....	3.9	4.8	7.1	8.2	8.0

NH_4 became almost negligible but the chlorine adsorption increased. Because of the high salt concentration with these hydroxides, the cataphoretic mobility could not be determined, but the following explanation will make the exchange reactions clear.

Hydroxides are formed by hydrolysis of the chlorides, and as has previously been pointed out in discussing the phenomenon of aging, the bonds must be co-valent, but the co-valencies change into electro-valencies at the isoelectric pH, at two different points in the colloid

$$X - O - H \rightleftarrows [X\,O]^- + H^+$$
$$\rightleftarrows [X]^+ + OH^-$$

and for the oxalate adsorption with the hydroxides of iron, aluminum, and chromium, this is true, as can be seen from the graphs. In an oxalate solution of high pH, the colloid lowers the pH of the solution but increases it if the oxalate solution had originally a low pH. The two dissociations must be equal at the isoelectric point, but because these hydroxides, if leached with a solution of barium acetate of a pH which is identically equal to their isoelec-

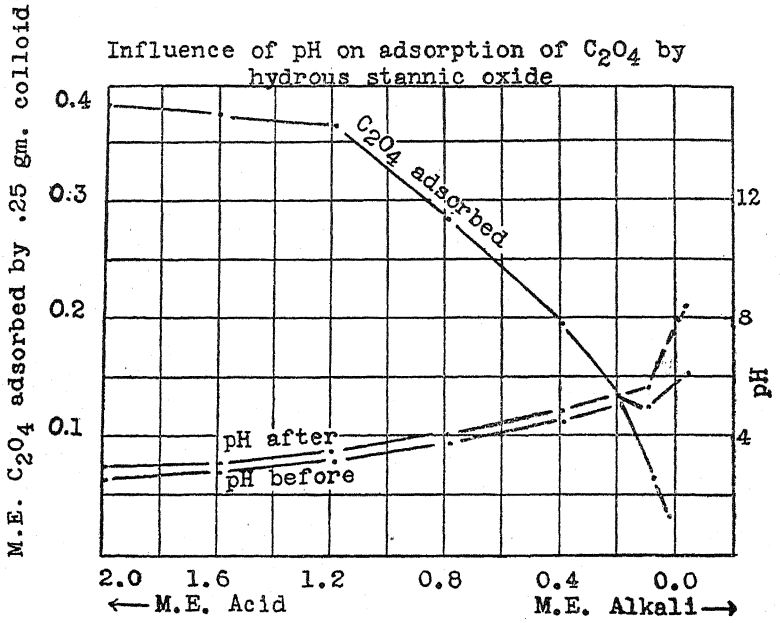


FIG. 1. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

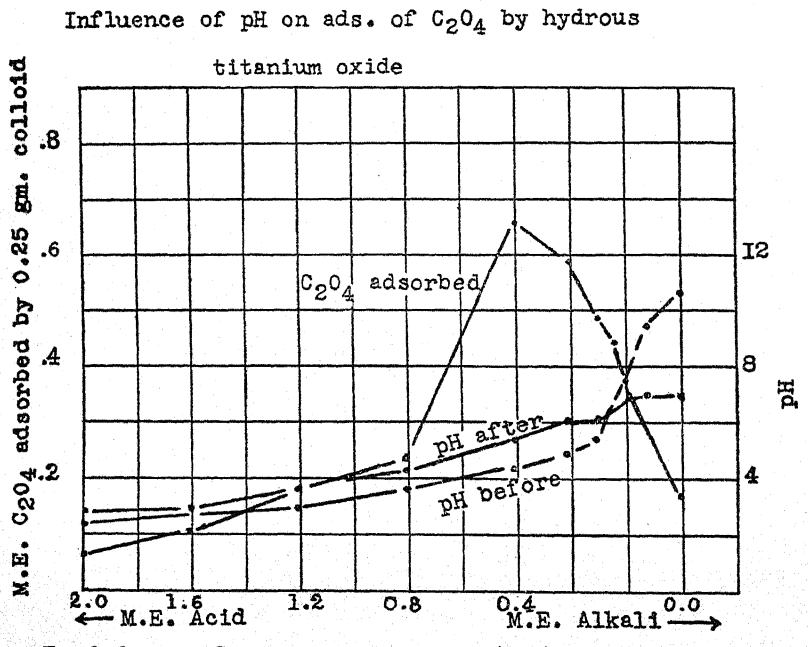


FIG. 2. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

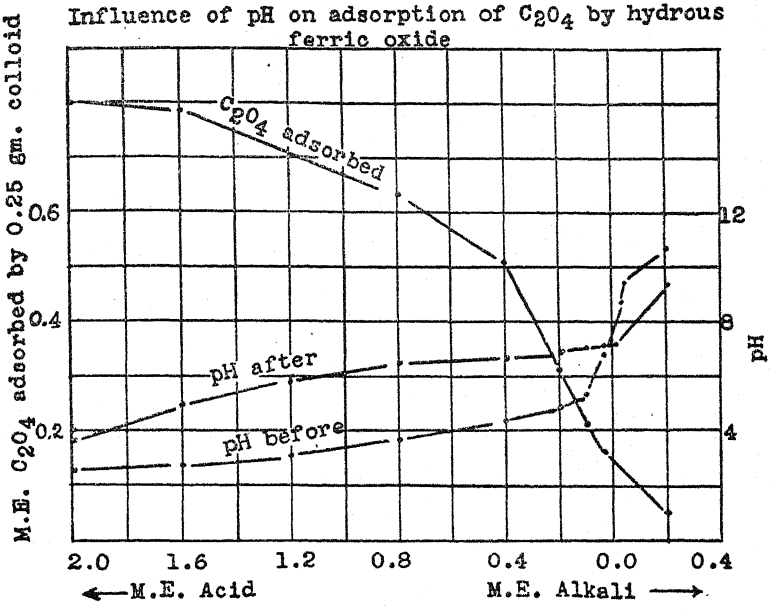


FIG. 3. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

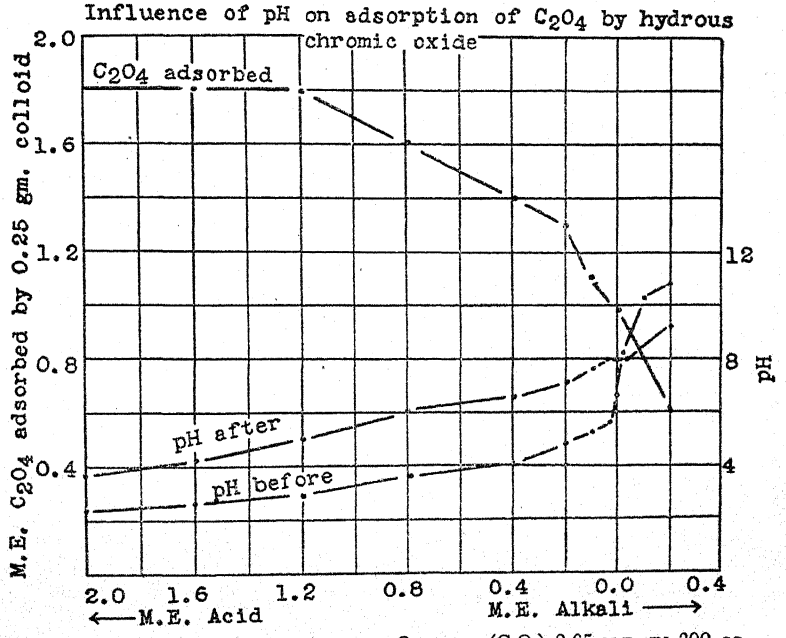


FIG. 4. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

tric pH, have no base exchange, the cationic ionization at the isoelectric point must be regarded as very small. Since the colloid has no charge at the isoelectric point, the anionic dissociation must also be equal to the cationic dissociation, and for both types of dissociation the total dissociation is at a minimum.

The lower the pH of the salt solution the greater will be the anionic dissociation, the hydroxyl ions forming a diffuse layer surrounding the positive micellae. When the concentration of oxalate ions is kept constant at all ranges of pH, the lower the pH the greater will be the ionic exchange of hydroxyl for oxalate ions, and other factors being equal, the greater the adsorption of oxalate ions; but the hydroxyl must first ionize, and this is controlled by the pH. The dissociation of hydroxyl ions is not, however, completely prevented until the

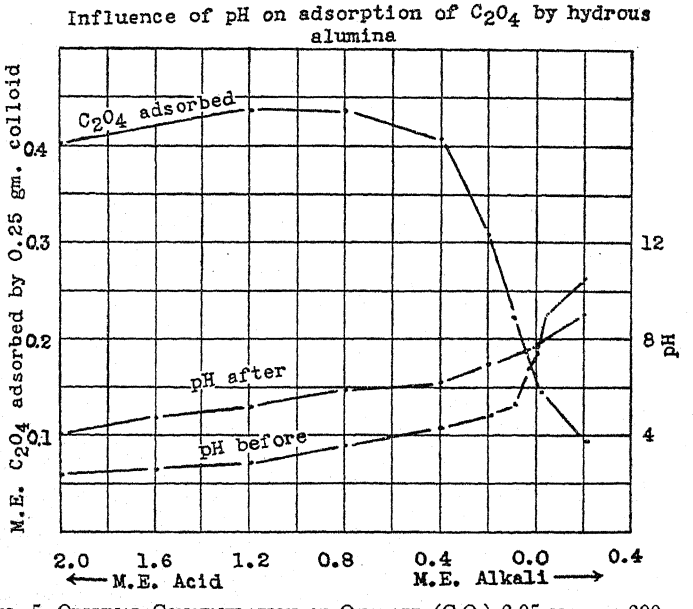


FIG. 5. ORIGINAL CONCENTRATION OF OXALATE (C_2O_4) 2.05 M.E. IN 200 CC.

pH of the salt solution is higher than the isoelectric pH, so that there is with oxalate solutions a slight adsorption of $C_2O_4^{=}$ above the isoelectric pH. The amount is, however, very small and hardly significant when working with very dilute solutions of oxalate as used in these experiments.

ADSORPTION AND SOLUBILITY

It has been found that the adsorption phenomena such as described in this paper are purely chemical in character, involving ionic exchange such as the replacement of the hydroxyl ion by the oxalate ion. With increasing ionic concentration the Freundlich adsorption isotherm does fit the adsorption extremely well, and Kolthoff (1) found that purely chemical reactions could be represented in such a manner. It is therefore necessary to derive the isotherm

by the aid of stoichiometry. He does this as follows. To start with a simple case, let us shake a slightly soluble salt, AB, with a solution containing C ions, which is capable of forming the slightly soluble compound AC. For example, let AgBr be shaken with a solution of thiocyanate. The reaction is as follows:

$$AgBr + CNS^- \rightleftarrows AgCNS + Br^-$$

If $K \cdot AgBr$ and $K \cdot AgCNS$ are the solubility products of AgBr and AgCNS, then the concentration of the silver ion is

$$[Br^-] = \frac{K\,[AgBr]}{K\,[AgCNS]} \times [CNS^-] = K_1\,[CNS^-]$$

Now Br^- is the quantity of bromide ion which went into solution and is therefore equal to the quantity of thiocyanate taken out of solution. This is equal to $\frac{x}{m}$ and the concentration of thiocyanate (CNS^-) remaining in solution is equal to the final concentration C.

Substituting in the foregoing equation we have $\frac{x}{m} = K_1\,C$ for monovalent ions. With the displacement of a divalent ion, by two monovalent ions, the equation is $\frac{x}{m} = K_1\,C^2$.

The magnitude of the coefficient K_1 depends on the solubility product of the slightly soluble compounds. With aluminum hydroxide and the adsorption of oxalate, the equation can be represented as follows:

$$Al_n(OH)_x + C_2O_4^= \rightarrow Al_n(OH)_{x-2}\,C_2O_4 + 2\,OH^-$$

but the solubilities of the hydroxide and the compound formed by adsorption of the oxalate are not the same, so that the law of diminishing adsorption with increasing pH does not strictly apply to either titanium or aluminum when oxalate is the ion adsorbed because of the secondary effect of solubility.

The increased solubility could be tested by determining the metallic ion in solution, but analytical difficulties in the absence of micro methods would be very great for small quantities. If another ion could be found which obeyed the law, then we would be safe in assuming that with oxalate adsorption solubility plays a very important part. In order to prove this the simultaneous adsorption of both oxalate and sulfate was studied with alumina and chromium hydroxide.

A quantity of sol was added to 250 cc. of a solution containing equivalent quantities of $SO_4^=$ and $C_2O_4^=$, the pH being varied by using sulfuric acid, sodium sulfate, sodium oxalate, and oxalic acid, all with equivalent concentrations of anions. The total volume in each case was made up to 500 cc., and the pH values before and after were determined colorimetrically. Equilibrium was established by hand shaking at frequent intervals over a period of 3 days.

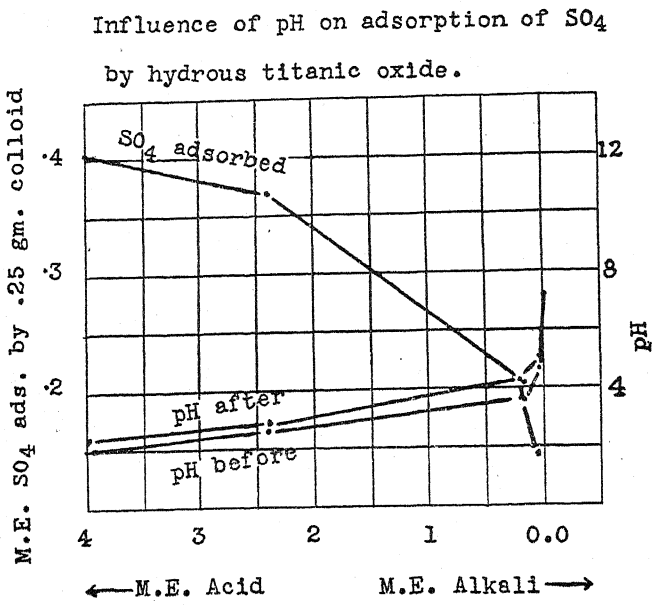


FIG. 6. ORIGINAL CONCENTRATION OF SO_4 4.0 M.E. IN 200 CC.

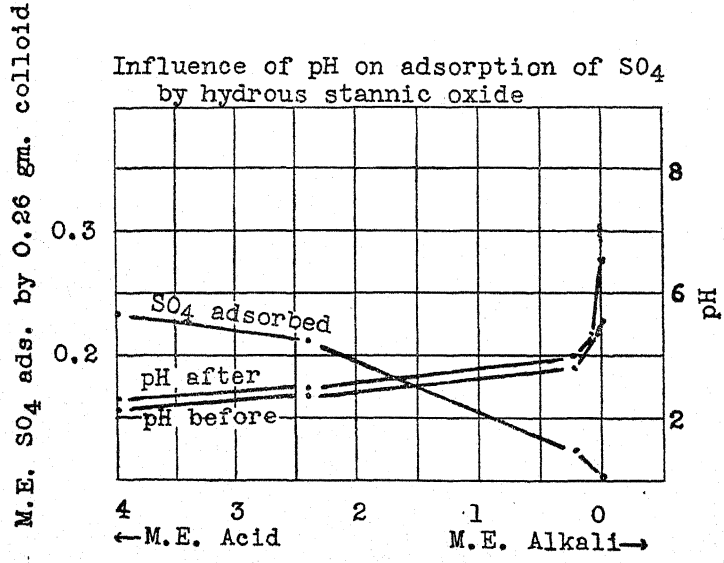


FIG. 7. ORIGINAL CONCENTRATION OF SO_4 4.0 M.E. IN 200 CC.

The oxalate was determined by titration with standard permanganate solution, and the sulfate determined in a separate aliquot by precipitation as barium sulfate in the presence of sufficient hydrochloric acid to prevent the precipi-

tation of barium oxalate. The results are represented graphically in figures 8 and 9.

While the oxalate adsorption still shows the same discrepancy, the sulfate adsorbed decreases consistently with increasing pH, in the same manner as the oxalate adsorption diminished with pH with the hydroxides of tin and iron. At a low pH the $SO_4^=$ is much more strongly adsorbed than the $C_2O_4^=$, but the reverse is true at the higher range of pH. Although it is usual to represent one ion as being more strongly adsorbed than another in colloid chemistry such as $C_2O_4^= > SO_4^=$, these results with hydroxides give no justification for such a procedure. Too many secondary reactions are obscured by such a method of presentation, not the least of which are the solubility effects and the great influence of pH.

With tin and titanium the simultaneous adsorption of both ions was not determined, but the adsorption of sulfate alone was studied. In the dry state neither of these two colloids adsorbs sulfate, but in the sol form there is a considerable adsorption of $SO_4^=$ below the isoelectric pH. The results are shown graphically in figures 6 and 7, and show again that the sulfate obeys the law, although with the oxalate adsorption by titanium, the secondary solubility effects are considerable.

EXCHANGE NEUTRALITY

With chromium, aluminum, and ferric hydroxide the point of exchange neutrality coincides with the isoelectric pH as previously determined. This is true whether the salt used is an oxalate or sulfate salt, and it is also, as has been found by Mattson and Hester, independent of the concentration of either salt or colloid. The figures show that the original concentration of $C_2O_4^=$ used was only 2.05 m.e. in 200 cc. with 0.25 gm. colloid. With the mixed solutions of oxalate and sulfate the concentration of sulfate and oxalate combined was 10 m.e. in 500 cc. with about 0.90 gm. of colloid. In the oxalate adsorption with tin and titanium hydroxide, the point of exchange neutrality does not coincide with the isoelectric pH, because of the comparatively strong buffering action of the oxalate solutions below pH 6.0, but the titanium hydroxide has its point of exchange neutrality at pH 4.8, the same as its isoelectric point, with sulfate solutions. The exchange neutrality determination for tin hydroxide with the sulfate solutions gave considerable difficulties, because of the grave salt errors to which indicators used at a low pH are subject, and the results for tin are subject to considerable error.

The point of exchange neutrality is, as can be easily seen from the graphs, independent of the concentration of either salt or colloid. It is also independent of the age of the colloid, for the cataphoretic mobilities are taken after the precipitates have stood overnight, but the exchange neutrality was determined with these hydroxides after the compounds had aged for over a week, and it occurs at the same pH whether the salt used is an oxalate or a sulfate, or a mixture of both.

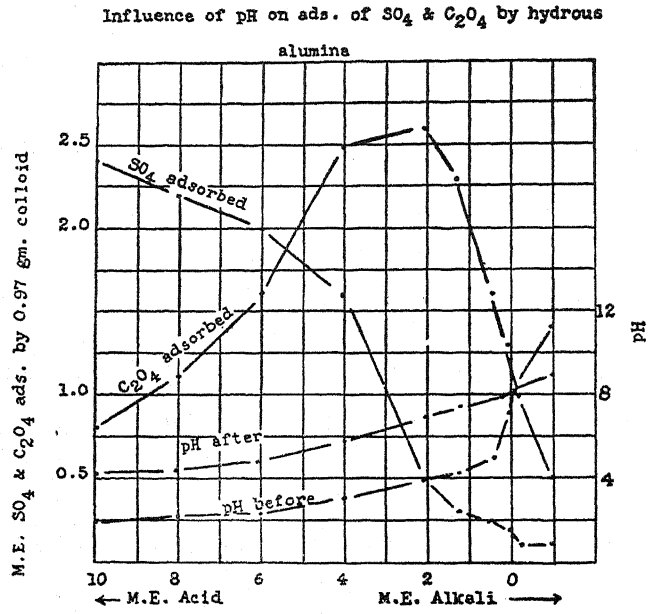


FIG. 8. ORIGINAL CONCENTRATION OF SO_4 PLUS C_2O_4 10.0 M.E. IN 500 CC.

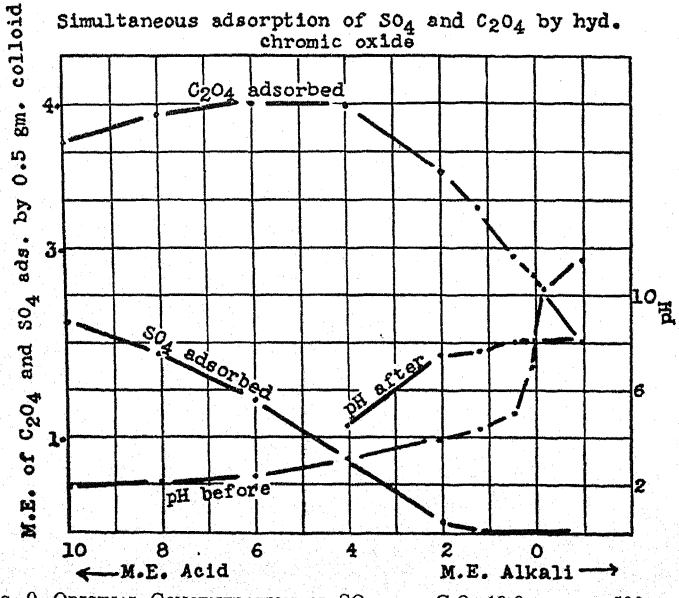
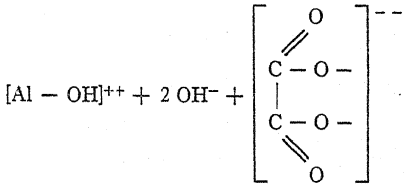


FIG. 9. ORIGINAL CONCENTRATION OF SO_4 PLUS C_2O_4 10.0 M.E. IN 500 CC.

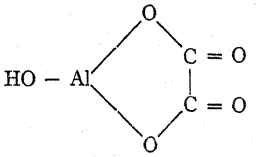
It is important to realize that the point of exchange neutrality as determined with a neutral salt solution refers only to the original compound and not to the new compound formed as a result of the ionic exchange, that is, when the C_2O_4 replaces the OH ion, the adsorption compound will have a new point of exchange neutrality, and an isoelectric point which will occur at a different pH. Substitution of a hydroxyl group by another ion gives, as would be expected, a compound which requires fewer hydroxyl groups to complete its micelle, and hence the isoelectric point of substituted hydroxides occurs at a lower pH.

The substitution of the hydroxyl group by the C_2O_4 ion can be represented most clearly by representing the colloid at the surface as $X - O - H$, which must of course be the case, as the colloids are formed by hydrolysis of the chlorides, the hydroxyl group replacing the chlorine. Taking aluminum hydroxide as an example, we find that the bonds of the anion chloride with the cation aluminum are changed on substitution of the chlorine by hydroxyl from electrovalent to co-valent form (5), and the hydroxide thus formed is isoelectric at pH 8.0. If leached with a solution of barium acetate, pH 8.0, it has no base exchange, but it does have a slight anion exchange, as seen in the graphs. With a solution the pH of which was originally above the isoelectric pH, the colloid dissociates H ions, thus lowering the pH.

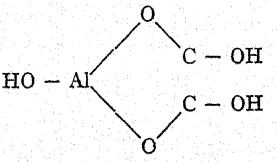
At a pH below its isoelectric pH the aluminum hydroxide would partially dissociate hydroxyl ions, and the oxalate ion would be substituted for it. Representing the ions in solution as follows, with the single bond representing two shared electrons and the double bond four shared electrons, we have:



These would combine to give a compound thus:



which would have a lower isoelectric pH, and it is probable that in a water medium the double bonds on adsorption of hydrions would rearrange to form single bonds:



This is again a co-valent compound, the necessary electrons coming from the lone pair of the oxygen of the oxalate ion. The hydroxyl ions are again at the surface, and the isoelectric point of this compound will also be the point where co-valencies change into electrovalencies, with an acid or alkaline dissociation, depending on the pH of the external medium.

That the point of exchange neutrality is independent of the quantity of adsorption and the nature of the salt can best be understood from this theory. The isoelectric point is that point at which the colloid is largely undissociated and in the co-valent state, with a minimum of the electrovalent form. Hydrions or hydroxyl ions are dissociated if the pH of the salt solution is removed from the isoelectric pH, the character of the dissociation changing, depending on whether the pH of the salt solution is above or below the isoelectric pH of the colloid. Not only the character of the dissociation but also the degree is a function of the pH. Substitution of anions or cations takes place as a secondary ionic reaction, and the amount of cations or anions adsorbed will depend on the concentration of the colloid and the salt, as well as the nature of the colloid and salt, and the solubility of the compound formed. It has been shown previously that the surface bonds are the same whatever the age of the colloid, so that the point of exchange neutrality must be the same whether the colloid be young or old. It is purely a function of the pH, and is that pH at which the dissociation of an amphoteric colloid is at a minimum, and also the pH at which the dissociation changes into an acid or alkaline dissociation, depending on the pH of the external medium.

BASE EXCHANGE

If the isoelectric tin and titanium hydroxides are leached with a normal solution of barium acetate, pH 7.0, they show considerable base exchange capacity, whereas ferric and aluminum hydroxides have none. That ferric and aluminum hydroxides have no base exchange at this pH is due to the fact that pH 7.0 is at or below the isoelectric pH of these compounds and the dissociation of hydrions is negligible. From the graphs it is seen, however, that both ferric and aluminum hydroxides dissociate hydrions if treated with a salt solution the pH of which is above the isoelectric pH. This is definite proof of a potential capacity for base exchange with these compounds, but leaching would have to be made with a salt solution of pH 10 or of a higher pH in order to have an appreciable base exchange. The divalent ions, such as calcium or barium, precipitate hydroxides at such high pH that they cannot be used, whereas the monovalent ions, sodium, potassium, or ammonium, form an exchange compound which is much too soluble with aluminum hydroxide, the so-called aluminates. Unless the pH of the leaching solution is also very carefully defined, it is, however, incorrect to state, as is frequently done, that aluminum hydroxide has no base exchange capacity.

SUMMARY

The influence of pH on the adsorption of oxalate and sulfate ions by various hydroxides has been determined, and the adsorption correlated with the isoelectric pH of the compounds. The lower the pH the greater the anion adsorption, which diminishes with increasing pH and reaches a low value at the isoelectric pH.

With the adsorption of the oxalate ion by aluminum and titanium, a secondary effect of diminished adsorption at low pH values was observed. This did not occur with the sulfate, and hence solubility is an important secondary reaction in ionic exchange reactions with colloids.

The point of exchange neutrality is independent of the concentration or the age of the colloid and of the salt used in so far as determined with solutions of oxalate and sulfate salts of different concentration.

REFERENCES

(1) KOLTHOFF, I. M. 1922 Die Electroadsorption als eine chemische Erscheinung. *Kolloid Ztschr.* 30: 35–50.

(2) MATTSON, SANTE. 1931 Laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311–331.

(3) MATTSON, SANTE. 1931 Laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 343–365.

(4) MATTSON, S. AND HESTER, J. B. 1932 Laws of soil colloidal behavior. X. Exchange neutrality and combining capacity. *Soil. Sci.* 34: 459–482.

(5) PUGH, A. J. 1933 Laws of soil colloidal behavior: XIV. Aging of colloids and base exchange. *Soil Sci.* 37: 403–427.



EFFECT OF BURNING ON FOREST SOILS[1]

H. A. FOWELLS AND R. E. STEPHENSON[2]

Oregon Agricultural Experiment Station

Received for publication September 5, 1933

Estimates place the area burned over annually by forest fires at seven million acres (4). Damage to the timber is seldom questioned. Damage to the soil through destruction of humus-making litter on the forest floor likewise appears to be a problem of importance. How much good humus material is destroyed and how much valuable plant food is lost annually by fires cannot be estimated.

Studies by other workers have indicated that the litter and partially humified material on the forest floor may contain 2 per cent or more of nitrogen (2). All the nitrogen is lost when organic matter burns. Under some conditions this loss may amount to several hundred pounds an acre, as indicated by work done in Minnesota (2).

There are, however, certain compensating effects which follow burning. Ash is liberated and becomes an immediate source of available nutrients. Burning destroys organic acids and liberates bases which further neutralize acids in the soil, thus improving conditions for biological processes and plant growth.

Decomposition of leaf litter or any high carbon material results usually in slow production of available nitrate. Fungi which are especially active in the "F" layer produce acids and thus discourage nitrate-forming organisms. Nitrifying organisms are most active in neutral or alkaline soils. These same fungi need nitrogen for their own cell protoplasm during growth. Any nitrate that is produced, therefore, is likely to be consumed by organisms.

Burning changes the soil flora and makes conditions favorable for bacteria rather than fungi. A different type of process therefore occurs. Probably more of certain nutrients become available for promotion of biological action and plant growth. The present paper deals with some of these questions.

METHOD OF STUDY

Four soils representing samples taken to a depth of 6 inches were studied. The soil, which was obtained from Alsea Mountain of the Coast Range in Western Oregon, has been classed as Olympic clay. Soil A was taken from a stand of young Douglas fir (*Pseudotsuga taxifolia* Lamb Britt) reproduction

[1] Published as technical paper No. 203 with the approval of the director as a contribution from the soils department, Oregon Agricultural Experiment Station.

[2] Graduate student in forestry and associate professor of soils, respectively.

about 10 years old. The ground cover was principally bracken fern (*Pteridium aquilinum pubescens* Underw.), with some leaf litter from such brush as vine maple (*Acer circinatum* Pursh) and hazel (*Corylus rostrata* Ait. Var. California A. DE.). Soil B was taken from an area heavily burned in the summer of 1932, when all litter was destroyed. Soils A and B were adjacent, being separated by the highway which stopped the fire. Soil C came from a stand of old growth Douglas fir with a dense ground cover of salal (*Gaultheria shallon* Pursh). Soil D was from a 1930 "burn" now covered with fire weed (*Epilobium angustifolium* L.), bracken fern, and salal.

Samples of each of the soils were weighed into tumblers in duplicate and treated as follows:

1. Nothing (check).
2. Sulfate of ammonia at the rate of 300 parts of nitrogen per million of soil.
3. Sulfate of ammonia at the same rate and precipitated calcium carbonate[3] at the rate of 2,000 pounds per million pounds of soil.
4. Ground Douglas fir litter at the rate of 5,000 pounds per million of soil.
5. Litter and sulfate of ammonia at the above rates.
6. Litter, sulfate of ammonia, and precipitated calcium carbonate at the same rates as above.

Twenty-five per cent of moisture was added to the air-dry soils, and the tumblers were incubated at room temperature for a period of 12 weeks. Moisture was maintained by frequent additions of water. At each interval of 4 weeks soil samples were drawn and nitrates determined by the phenoldisulfonic acid method. At the end of the period water-soluble calcium and potassium were determined. On some of the samples (as shown in the tables) water-soluble phosphate was determined. On other samples phosphate soluble in 0.002 *N* $(NH_4)_2SO_4$ buffered to pH 4.0 was obtained by the same colorimetric method (6).

RESULTS OF NITRIFICATION STUDY

The data from the nitrification study are presented in table 1. The results represent the average of duplicate treatments.

In both the burned soils and for every treatment, nitrification started much better and continued more rapidly throughout the period of 12 weeks. The difference between the burned and the unburned is very marked. The data indicate that the supply of basic material is one important reason, though probably not the only one, for the difference. By comparing treatments 2 and 3 and 5 and 6, which are alike except for the addition of the basic material calcium carbonate, it is found that lime has increased nitrification very appreciably. On the burned soils the added lime approximately doubled nitrification as an average for the period, whereas on the unburned the increase was roughly 10-fold.

[3] The calcium carbonate will be called "lime" for convenience in the remainder of this paper.

The addition to the soil of litter alone or with ammonium sulfate did not have a very marked effect on nitrification by the burned soils. On the unburned soils the extra litter stimulated nitrification in every case. Gibbs and

TABLE 1

Nitrates as p.p.m. of nitrogen in the soil

SOIL USED	TREATMENT					
	1 Check	2 $(NH_4)_2SO_4$	3 Lime $(NH_4)_2SO_4$	4 Litter	5 Litter $(NH_4)_2SO_4$	6 Litter, Lime $(NH_4)_2SO_4$
Soil A, young reproduction:						
4 weeks	Trace	Trace	Trace	Trace	Trace	Trace
8 weeks	Trace	2.9	20	Trace	5.5	22.2
12 weeks	Trace	5.1	33.3	1.4	20.9	100.0
Totals	Trace	8.0	53.3	1.4	26.4	122.2
Average	Trace	2.7	17.8	0.5	8.8	41.7
Soil B, recent burn:						
4 weeks	7.2	5.3	28.8	7.6	3.3	26.1
8 weeks	30.9	28.6	110.0	33.3	27.7	110.0
12 weeks	36.5	61.7	100.0	30.6	51.5	100.0
Totals	74.6	95.3	238.8	71.5	82.5	236.1
Average	24.9	31.8	79.6	23.8	27.5	78.7
Soil C, old-timber:						
4 weeks	Trace	Trace	Trace	Trace	Trace	4.4
8 weeks	4.7	Trace	32	18.3	1.9	59.3
12 weeks	18.3	3.1	30	29.1	6.0	120.0
Totals	23.0	3.1	62	47.4	7.9	283.7
Average	7.7	1.0	21	15.8	2.6	61.2
Soil D, 2 year-old-burn:						
4 weeks	19.3	20.8	43.8	21.0	24.0	55
8 weeks	40.1	54.5	120.0	40.0	60.8	110
12 weeks	29.4	76.4	123.6	44.4	84.0	146
Totals	88.8	151.7	287.4	105.4	168.8	311
Averages	29.6	50.6	95.8	35.1	56.3	103.7
Average of "Burned over"	27.2	41.2	87.7	29.4	41.9	91.2
Average of "Unburned"	3.9	1.8	19.4	18.2	5.7	51.4
Average of all Soils	15.6	21.5	53.6	18.8	23.8	71.3

Werkman report that forest litter reduced nitrate production and that fern residues had but little inhibiting effect (3). The reason for the stimulation of nitrate production by the litter on these unburned soils is not known. Perhaps the litter may have resulted in ammonification, and the ammonia thus

produced served as basic material to stimulate nitrate formation. It is generally conceded that ammonia is produced rather abundantly in the humification of forest litter. Since tests for ammonia were not made, however, this cannot be verified.

The unburned soils were very slow in starting nitrification. This is true regardless of the addition of basic material. In the burned soils nitrification, as far as the data indicate, was about at a maximum at the end of 8 weeks. In the unburned soils nitrification was still improving at the end of 12 weeks and yet was far behind the burned soils in most cases. Evidently nitrifying organisms were favored by burning.

The most effective treatment for nitrification was a combination of litter, lime, and ammonium sulfate. The litter may introduce organisms, lime supplies base, and ammonium sulfate furnishes an easily nitrifiable form of nitrogen. With this combined treatment, after 12 weeks the unburned soils nitrify nearly as well as the burned.

Under natural conditions growth depends very largely upon the supply of nitrogen. Forest trees, however, may be able to use nitrogen in the ammonia form as well as in the form of nitrate. There must be a source of nitrogen, however, before ammonia can be produced. This source is principally the decomposing litter on the forest floor.

RESULTS OF STUDY OF SOLUBLE BASES

The effect of nitrification upon the solubility of soil bases is shown in table 2.

The data indicate that soluble calcium parallels in a general way the amount of nitrate produced. Of course the addition of lime has a bigger effect than any other treatment upon soluble calcium. However, the amount of soluble calcium is much higher in the burned soils than in the unburned where lime is not used. Since lime is an important ash constituent such a result may be expected. The addition of litter did not have much effect in increasing available calcium, as it likewise had little effect on nitrification.

The soluble potash is increased in most cases by the addition of ammonium sulfate. The addition of lime had little effect upon soluble potash. Soluble potash does not parallel the nitrates so closely as does the soluble calcium. Litter had almost no effect in increasing soluble potash. In the determination of soluble potash ammonia was eliminated by evaporation and burning.

The water-soluble phosphate is low and about the same in amount with all treatments, probably because of the strong phosphate-fixing power of these soils. However, burning liberates phosphate in the ash, and phosphate so liberated should become acid soluble. When the unburned and burned soils are compared there is consistently somewhat more acid-soluble phosphate in the latter. The largest amount of acid-soluble phosphate in the unburned soils was after the old burn, 61 p.p.m. Apparently nitrification has very little effect in increasing phosphate availability.

The data would indicate that regardless of how well trees may be able to

utilize the ammonia form of nitrogen, the process of nitrification should be favorable to good tree nutrition. The increased supply of available bases

TABLE 2.

Water-soluble bases as p.p.m. of the ion of the soil

SOIL	NUTRIENTS*	TREATMENT					
		1 Check	2 $(NH_4)_2SO_4$	3 Lime $(NH_4)_2SO_4$	4 Litter	5 Litter $(NH_4)_2SO_4$	6 Litter, Lime $(NH_4)_2SO_4$
A. Young reproduction	Ca†	4.0	40.0	248.0	4.0	42.0	248.0
B. Recent burn	Ca	55.0	150.0	270.0	40.0	100.0	270.0
C. Old timber	Ca	13.0	Lost				
D. 2-year-old burn	Ca	25.0	150.7	271.2	37.5	158.1	331.5
Average	Ca	28.0	113.6	263.1	27.2	100.0	283.2
A Young reproduction	K‡	8.5	59.6	59.6	7.1	78.1	76.7
B. Recent burn	K	26.9	52.5	46.9	23.1	58.0	51.1
C. Old timber	K	26.9	39.8	55.4	39.8	52.5	52.5
D. 2-year-old burn	K	42.6	83.8	85.2	56.8	95.1	99.4
Average	K	26.2	58.9	61.8	31.7	70.9	70.0
A. Young reproduction	PO_4	0.23	0.23	0.23	0.23	0.23	0.23
B. Recent burn	PO_4	0.23	0.23	0.23	0.23	0.23	0.23
	ACID-SOLUBLE						
C. Old timber	PO_4	31.0	31.0	36.0	32.0	29.0	28.0
D. 2-year-old burn	PO_4	39.0	44.0	44.0	39.0	36.0	36.0
	LAST SAMPLING NITRATE						
A. Young reproduction	N	Trace	5.1	33.3	1.4	20.9	100.0
B. Recent burn	N	36.5	61.7	100.0	30.6	51.5	100.0
C. Old timber	N	18.3	3.1	30.0	29.1	6.0	120.0
D. 2-year-old burn	N	29.4	76.4	123.6	44.4	84.0	146.0
Average	Nitrate	21.2	36.6	71.7	26.4	40.6	116.5

Acid-soluble phosphate on soils A and B was 31 and 61 p.p.m. respectively.

* Nutrients are water-soluble unless otherwise indicated.

† Calcium was precipitated as oxalate and titrated with permanganate.

‡ Potash was determined by the cobaltinitrite method.

resulting from the nitrification process in a base-poor soil must be helpful. Any strong acid such as nitric or sulfuric produced by biological processes is

effective in dissolving bases. An equivalent amount of sulfuric acid is always liberated from the ammonium sulfate, when the ammonia is changed to nitric acid by nitrification.

GENERAL EFFECT OF BURNING

The forest tree depends for its nutrition largely upon the mineralization of the litter dropped upon the forest floor. Most of the humus material and the humification processes occur on top of the soil. As the process continues some of the soluble humus is leached into the topsoil, which is very porous and absorptive to a depth of 6 inches or more.

When fire enters the forest, both the litter and the humifying material are consumed at once. Even the humus in the immediate surface soil may be partly burned out. This is indicated in the data in table 3.

In the area burned over to dispose of slash, the humus content of the soil is low in the immediate surface and increases with depth. In the unburned area the humus content of the soil surface is high, and decreases with depth.

TABLE 3

*Humus content expressed as per cent of soil**

	DOUGLAS FIR UNBURNED PER CENT HUMUS	HEAVILY BURNED AREA PER CENT HUMUS
Surface inch	4.86	1.70
4½-inch to 7½-inch depth	4.81	3.78
10½-inch to 12½-inch depth	3.77	4.47

* Humus was determined by the modified Rather method (1).

These data of course do not take into consideration the actual litter and humus on top of the unburned soils.

The data of this work indicate that the immediate effect of burning is to produce a rather liberal supply of plant food. This is favorable both to soil organisms and to plants growing on the soil. Just after a burn which destroys the over growth there is likely to follow a rather profuse vegetation of wild grasses and herbs that produce excellent humus materials. Even legumes may volunteer. It is well known that clover starts easily when seeded in the ash after a burn. Leaving out of consideration damage that is done the trees, should the burn occur only once, or very infrequently, the effect upon soil fertility might not be very disastrous.

Nevertheless, what represents several years of leaf fall is entirely consumed by fire in a few minutes. Data collected by the senior author indicate that in this section in young forest there may be 10 tons or more of litter and humus material per acre on the forest floor. In old forests there are several times as much. More than 100 tons per acre has been reported (5).

In timber that is so dense as to prevent growth of grass, the renewal of so much humus material would require several years. The litter fall per season

probably does not exceed 2 tons and may be considerably less. Repeated burning, therefore, must soon result in a condition where there is no longer any organic materials in the soil to humify. Nature's method of renewing forest soils then becomes inoperative. Only one result can follow. Impoverished soils must lead to reduced tree growth, through lack of nutrients, reduced moisture capacity, and generally unfavorable conditions. It would seem rather dangerous to conclude, therefore, that because the immediate effect of burning is helpful the general practice even with controlled fires repeated frequently would be beneficial to the soil.

CONCLUSIONS

Nitrification in forest soils is stimulated by burning and the liberation of the basic ash materials.

Burning and the increased nitrification increase the soluble mineral nutrients in the soil, probably for some time after burning.

Burning destroys not only the organic matter on top of the soil, but may destroy some of that in the immediate soil surface.

The temporary effect of burning may be helpful at least in some respects, but, since the productivity of the forest soil depends upon gradual mineralization of the fallen litter, it does not appear reasonable to expect continuous and often repeated burning to improve forest soil fertility.

REFERENCES

(1) ALEXANDER, L. T., AND BYERS, H. G. 1932 A critical laboratory review of methods of determining organic matter and carbonates in soil. *U. S. Dept. Agr. Tech. Bul.* 317: 18–19.

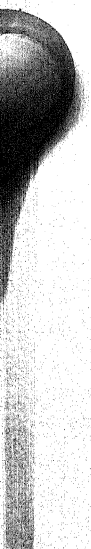
(2) ALWAY, F. J., AND MCMILLER, P. R. 1933 The floor of some northern Minnesota forests. *Amer. Soil Survey Assoc. Bul.* 14: 11–13.

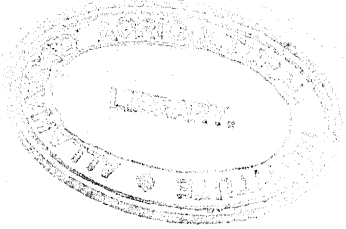
(3) GIBBS, WM. W., AND WERKMAN, C. H. 1922 Effect of tree products on bacterial activities in soil: I. Ammonification and nitrification. *Soil Sci.* 13: 303–322.

(4) GREELEY, W. B. 1924 Idle land and costly timber. *U. S. Dept. Agr. Farmers' Bul.* 1417.

(5) LUNT, H. A. 1933 Factors affecting the density of forest soil profile horizons. *Amer. Soil Survey Assoc. Bul.* 14: 16–18.

(6) TRUOG, E. 1930 The determination of readily available phosphorus in soils. *Jour. Amer. Soc. Agron.* 22: 874–882.





INFLUENCE OF TEMPERATURE ON BACTERIAL NITRIFICATION IN TROPICAL COUNTRIES

S. P. TANDON AND N. R. DHAR

Allahabad University, India

Received for publication September 27, 1933

In previous communications (2, 3, 5) from these laboratories it has been stated that in tropical countries ammonification and nitrification in soil are mainly due to the photo-oxidation of amino acids to ammonia and of ammonium salts to nitrite and nitrate by the oxygen of the air. In order to throw more light on the mechanism of nitrification in soils of tropical countries, we have undertaken an investigation of the velocities of bacterial nitrification at various temperatures.

EXPERIMENTAL

A pure culture of nitrite-forming bacteria was prepared from garden soil by Omeliansky's method of elective culture, the medium employed being

Ammonium sulfate	2 to 2.5 gm.
Potassium phosphate	1 gm.
Magnesium sulfate	0.5 gm.
Sodium chloride	2 gm.
Ferrous sulfate	0.4 gm.
Distilled water	1,000 cc.
Magnesium carbonate	excess (0.5 gm. per 50 cc. of the medium)

Fifty cubic centimeter portions of this medium were taken out in 200-cc. Jena glass flasks, which were plugged with absorbent cotton and sterilized at 20 pounds pressure for 15 minutes. The ammonium sulfate was sterilized separately as a 10 per cent solution, and the required amount was added, with a sterile pipette, to the sterile flasks containing the other constituents of the medium.

One gram of the garden soil was inoculated into the flasks containing the culture medium and the flasks were then incubated at 30° to 35°. After a week, growth of the bacteria began and was indicated by the appearance of nitrite and disappearance of the ammonium salt. When all the ammonium salt was oxidized to nitrite, a fresh portion of ammonium sulfate was added. This second portion was oxidized much more rapidly, since the nitrite-forming bacteria had developed abundantly. After several additions of ammonium sulfate, a vigorous culture of the specific organisms was obtained. Now a drop of the suspension from the bottom of the flask was transferred to another flask

containing the same medium. After four or five such transfers, the culture obtained was fairly pure and rich enough in the specific organisms and was used for isolation purposes. In order to get the culture absolutely pure, a drop or two from the bottom was plated on a silica gel contained in a petri-dish, which was kept inverted in an incubator at 35°. The colonies developed after 15 days, and a single selected colony was inoculated into a fresh medium. The culture of the bacteria thus obtained was quite pure.

For the systematic study of bacterial nitrification, the following procedure was adopted. Various sets of experiments were thus arranged:

Solution A—10 per cent sterilized ammonium sulfite.
Solution B—containing other constituents of the medium in the proportions already stated.

Seventy cubic centimeters of solution B were taken in 250-cc. Jena glass conical flasks and 0.5 gm. magnesium or calcium carbonate added to it. The flask was then sterilized at 20 pounds pressure in an autoclave. Into each flask was introduced 2 cc. of the purified culture suspension after thorough shaking. The culture suspension was freed from traces of nitrite by repeated washing with sterilized distilled water. Two flasks under identical conditions were then kept in a thermostat at a definite temperature and the mean of the two results obtained with the two flasks was taken in order that the experimental error might be minimized. A control experiment under similar conditions but containing no bacteria was always conducted side by side at the same temperature. The amount of nitrite formed was estimated by a Duboscq colorimeter from time to time using a mixture of 0.8 per cent solution of sulfanilic acid in acetic acid of sp. gr. 1.04 and 0.5 per cent solution of α-naphthylamine in acetic acid of the same specific gravity as the indicator (colorimetric determination according to Griess-Ilsovay method). Equal amounts of the indicator were added both to the nitrite solution of the unknown strength and to the standard nitrite solution, and the color of the two was matched in the colorimeter. The amount of nitrite formation was taken to be directly proportional to the activity of the organisms. The experimental results obtained with $MgCO_3$ are recorded in table 1.

At 50° the amounts of nitrite formed in the flasks containing the bacteria were the same as in the control flasks containing no bacteria.

The results recorded in table 1 clearly show that the optimum temperature of nitrification with the tropical nitrite-forming bacteria is about 35°. The experiments of other workers, such as Omeliansky and Winogradsky, carried on in colder countries show that the optimum temperature is near 25° for the nitrite-forming bacteria. This clearly brings out the fact that the nitrite-forming bacteria possess the capacity of adapting themselves to changed surroundings. On account of the high temperatures existing for the greater part of the year in the tropics, the bacteria in soils of tropical countries have so modified themselves as to thrive best at 35°. It is interesting to note that

Panganiban (6), working in the Philippines, has also observed an optimum temperature of 35° with his nitrite-forming bacteria.

At temperatures lower than the optimum, a regular rising curve is obtained when the amount of nitrite formed is plotted against time. At the optimum temperature, where the activity of the bacteria is at the highest, nitrite is rapidly formed in the beginning and, as the concentration of the ammonium salt left is decreased, the velocity of nitrification is also diminished. In such cases, as is to be expected, an S-shaped curve is obtained.

Table 1 shows that at 0° the bacteria are capable of maintaining life activity for some days in the beginning, but a prolonged exposure to this temperature ultimately results in the complete stoppage of their life activity. Such a culture when brought back again to optimum conditions fails to show any further sign of growth even after being kept for 9 months. From these experiments we conclude that at 0° complete destruction of the bacteria occurs within

TABLE 1

Amount of nitrite formed at various temperatures

(Gm. of NO_2 per liter)

TIME	NITRITE FOUND AT TEMPERATURE OF						
	0°	15°	20°	25°	30°	35°	40°
hours							
67	0.000253	0.0001525	0.001169	0.005066	0.00792	0.008848	0.00064
115	0.000281	0.0002884	0.00175	0.008505	0.02304	0.0438	0.000689
163	0.000281	0.0004045	0.002779	0.01777	0.0497	0.09385	0.000844
187	0.000281	0.0006595	0.002953	0.02656	0.0673	0.1438	0.000950
211	0.000281	0.001318	0.00376	0.0386	0.08503	0.1987	0.001076
235	0.000281	0.002163	0.004468	0.05797	0.1026	0.2715	0.00141
259	0.000281		0.00559	0.08585	0.12595	0.3585	0.001718

a few days. At 50° also we find that the bacteria are incapable of existence, as at this temperature our experiments gave equal amounts of nitrite formation both in the control flasks and in those containing the bacterial culture.

It has been reported by various investigators that calcium or magnesium carbonate is essential for the activity of the nitrifying bacteria. The function of the carbonate is twofold: firstly, it acts as a neutralizer of the acidity developed in the solution due to the oxidation of ammonium salts and thus maintains a constant pH value; and secondly, it supplies the organisms with their carbon requirements for the building up of their body.

Ashby (1) has found that nitrification proceeds more rapidly in the presence of magnesium carbonate than in the presence of calcium carbonate. This observation is also confirmed by S. Machida, who found nitrification to be favored more by magnesium carbonate than by calcium carbonate. In table 2 we are recording our results with both these carbonates.

These results show that the activity of our bacteria is higher in the presence

of calcium carbonate than of magnesium carbonate. Winogradsky has reported that an excess of free ammonia is detrimental to the growth and activity of nitrifying bacteria. We know that the medium becomes more alkaline in the presence of magnesium carbonate, which therefore liberates more ammonia, and hence the activity of the bacteria is considerably diminished. Calcium carbonate, on the other hand, does not impart so much alkalinity to the medium. This is probably due to the greater solubility of magnesium carbonate than of calcium carbonate. The smaller velocity of nitrification in the presence of magnesium carbonate may not be wholly due to increased alkalinity of the medium. From our experiments calcium carbonate appears to be about four to five times more efficient than magnesium carbonate. It appears that the calcium ions present in the system containing calcium carbonate may exert a specific action on the bacterial growth.

TABLE 2

Amount of nitrite formed at 30°

(NO_2 in gm. per liter)

TIME	NITRITE FOUND	
	With calcium carbonate	With magnesium carbonate
hours		
67	0.04379	0.00792
115	0.1178	0.02304
163	0.2084	0.0497
187	0.2649	0.0673
211	0.3415	0.08504
235	0.4326	0.1026
259	0.5075	0.1259

Solution A—3 cc. (10 per cent sterilized ammonium sulfate).
Solution *B*—70 cc. (containing other constituents of the specific medium and sterilized).
0.5 gm. magnesium or calcium carbonate.
Bacterial culture—2 cc. suspension.

Last summer, in the month of April, the soil temperature at Allahabad rose to 50° at 2 inches deep. May and June of 1933 were frequently cloudy, and the summer was a mild one.

Leather, working at Pusa, India, stated that the maximum temperature at Pusa may rise to 70° at the soil surface and 60° at a depth of 1 or 2 inches. In Egypt the recorded temperature is 65° at the surface and 56° at a depth of 2 inches. From our measurements on the influence of temperature on bacterial nitrification, we find that 35° is the optimum temperature for bacterial nitrification, which becomes practically negligible at 50°. Hence in tropics, nitrification in soil cannot be to any extent, of bacterial origin in the months of April, May, June, and July, when the soil temperature is much greater than the optimum for nitrification by bacteria. In these very months the amount of nitrate in soil is, however, the greatest (5). Even in colder countries, like

England and Germany, the soil temperature may rise to 35° or more in summer (8), although the optimum temperature for bacterial nitrification is stated to be 25°. In these countries bacterial nitrification must be greatly reduced in the summer months as a result of the soil temperature becoming much greater than the optimum temperature for bacterial nitrification, though the nitrate content of the soil in these countries is also largest in the summer time.

Dhar and Atma Ram (4) have shown that in the photo-oxidation of organic substances, specially of the amino acids and hydroxy compounds, appreciable amounts of formaldehyde are formed. The formaldehyde produced in the photo-oxidation of organic compounds present in the soil is likely to hinder the bacterial processes taking place in the soil, and hence the ammonification and nitrification in the soil due to bacteria will be curtailed by the presence of the formaldehyde, which is a powerful antiseptic and is produced in soil by the oxidation of the organic compounds by air in the presence of light.

In a private communication to one of the authors, Dr. A. S. Corbet, working at the Agricultural Research Station, Bracknell, Berkshire (England), makes the following statement: "From my experience in Malaya, where I was particularly struck by the paucity of soil microörganisms, I should think your results on photonitrification are of quite general application in tropical countries."

In the unmanured soil of the Institut de Brie-Comte-Robert, Winogradsky found only a few living organisms, three or four kinds of cocci, a few azotobacter, some mycelium of actinomyces, and a few yeast, but no bacilli or moulds. These are regarded by Winogradsky as the normal population of the soil. It is believed that in moist soils, most of the bacteria are concentrated in the first 2 feet of soil. The largest numbers are observed 1 to 3 inches below the surface. Because of the antiseptic properties of the solar radiations and the rapid evaporation of moisture from the soil surface, the number of bacteria is less on the surface. According to Waksman (9), soils under shade have the highest number of bacteria at a depth of 1 inch, and the numbers decrease with depth, whereas soils receiving sunlight contain the largest numbers of bacteria at a depth of 4 inches.

Recently it has been observed by us that dilute solutions of sodium or potassium nitrite are almost completely oxidized to nitrate when exposed to light along with solid substances like TiO_2, ZnO, Fe_2O_3, and sterilized soil in the absence of bacteria. In other words, from the experimental work carried on in these laboratories we find that not only are ammonium salts oxidized to nitrate by air in the presence of light but the nitrites are also, in their turn, readily converted into nitrate when exposed to light and air along with the photocatalysts. It seems, therefore, that the whole process of nitrification can be photochemical. Moreover it has been found by us that solutions of amino acids are readily oxidized to ammonia in the presence of air and light. Thus one of the important stages in the process of ammonification is also markedly accelerated by light.

The increase in fertility of soil as a result of exposure to sunlight as practiced in India, Egypt, and other countries from time immemorial can be easily explained from our observations. The increased production of ammonia and nitrate by partial sterilization of soil has been stated by authorities on agriculture to be not a necessary consequence of the higher number of the organisms present in the soil. As nitrification is essentially an oxidation reaction taking place on the soil surface, the various agencies: e.g., increase in the aeration, soil surface, and temperature up to a limiting value, will increase nitrification. Moreover sunlight or diffused light is always available and accelerates the formation of NH_3 from amino acids and the oxidation of NH_3 to nitrite and of nitrite to nitrate. It appears that the increase in fertility of soil on heating or exposure to sunlight, as is done by cultivators in many countries, is mainly due to increased oxidation of nitrogenous compounds, especially of the amino acids, causing the formation of NH_3 and to increased nitrification brought about by the soil becoming more porous and by the accentuation of the air supply and above all by the increased light absorption. When a soil is ploughed, fresh surfaces are exposed to sunlight and air and nitrification is facilitated.

It is generally agreed that nitrification is most active at the surface of the soil. According to Prescott and Piper (7) nearly 80 per cent of the nitrate accumulation takes place in the first $3\frac{1}{2}$ inches of the soil from the surface. From the observations recorded in this paper it seems to us that the soil temperature in the summer months in tropical countries must not be much below 50° even at the depth of $3\frac{1}{2}$ inches from the surface, although the bacterial nitrification has the optimum temperature of 35°. In Lyallpur, Punjab, in summer months, the soil temperature at 5 cm. depth is as high as 50° and at 30 cm. depth 37°. It appears, therefore, that in the first $3\frac{1}{2}$ inches of the soil, where there is maximum nitrification as observed by different investigators, very few bacteria can exist in tropical countries in summer months, although the amount of nitrate in soil is maximum in summer. We are led to conclude, therefore, that agencies other than bacterial must be active in causing nitrification, which is going on at a maximum speed in the soil in summer months within $3\frac{1}{2}$ inches of the soil. As we have observed that light markedly accelerates the oxidation of amino acids to NH_3, of ammonium salts to nitrites, and of nitrites to nitrates and that all these oxidations are accelerated by increase of temperature, we are led to believe that light absorption and increase of temperature play a more important rôle than bacteria in nitrification in summer months, when the nitrate content of the soil is known to be maximum in almost all countries.

In publications from these laboratories it has been shown that the oxidation of ammonium salts mixed with sterilized or unsterilized soil in covered vessels coated with Japan black enamel (i.e., receiving no light) when kept in the sun along with the vessels receiving light is much smaller than in those exposed to light. If nitrification were mainly a bacterial process the amount of nitrifica-

tion in the vessels in the dark with the unsterilized soil should not have been materially different from those exposed to light. We have made numerous comparative experiments like those on the oxidation of ammonium salts to nitrite and of nitrite to nitrate with both sterilized and unsterilized soil kept in light and in dark and we find that the formation of nitrite and nitrate is always much greater in the vessels exposed to light than in those kept in the dark.

From all the points discussed in this paper it appears to us that the process of nitrification in soil under ordinary conditions is due more to sunlight than to bacteria, especially in tropical countries.

SUMMARY

The optimum temperature of the nitrite formers in tropical soil is 35° as against 25° observed in the soil of temperate countries.

The velocity of bacterial nitrification is greater in the presence of calcium carbonate than in the presence of magnesium carbonate.

The soil temperature in tropical countries in summer markedly exceeds the optimum temperature for bacterial nitrification and may even be greater than the maximum temperature at which the nitrite-forming bacteria can exist. Hence in summer, nitrification in tropical soil cannot be mainly due to bacteria.

The amount of nitrate in soil is maximum in summer, and as most of the bacteria are likely to be killed by the high temperature prevailing in the soil, it is concluded that light plays an important rôle in nitrification in soil.

REFERENCES

(1) ASHBY, S. F. 1907 Some observations on nitrification. *Jour. Agr. Sci.* 2: 52.

(2) DHAR, N. R., BHATTACHARYA, A. K., AND BISWAS, N. N. 1933 Photonitrification in soil. *Soil Sci.* 35: 281.

(3) DHAR, N. R., BHATTACHARYA, A. K., AND BISWAS, N. N. 1933 Influence of light on ammonification and nitrification in soil. *Jour. Indian Chem. Soc.* 10: 699.

(4) DHAR, N. R., AND RAM, A. 1933 Presence of formaldehyde in rain and dew and the problem of carbon assimilation. *Jour. Indian Chem. Soc.* 10: 287.

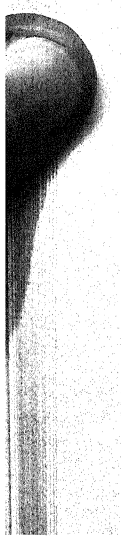
(5) DHAR, N. R., AND RAO, G. G. 1933 Nitrification in soil and air—a photochemical reaction. Rây Comm. Vol., *Jour. Indian Chem. Soc.* 81.

(6) PANGANIBAN, E. H. 1925 Temperature as a factor in nitrogen changes in the soil. *Jour. Amer. Soc. Agron.* 17: 1.

(7) PRESCOTT, J. A., AND PIPER, G. R. 1930 Nitrate fluctuations in a South Australian soil. *Jour. Agr. Sci.* 20: 517.

(8) RUSSELL, E. J. 1932 Soil Condition and Plant Growth, ed. 6. Longmans, Green & Co., London, New York, Toronto.

(9) WAKSMAN, S. A. 1916 Studies in soil protozoa. *Soil Sci.* 1: 135; 2: 363.



MICROBIAL ACTIVITIES IN SOIL: I. NITROGEN FIXATION BY AZOTOBACTER AND ACTIVITY OF VARIOUS GROUPS OF MICROBES IN PALOUSE SILT LOAM[1]

S. C. VANDECAVEYE AND B. R. VILLANUEVA[2]

Washington Agricultural Experiment Station

Received for publication October 2, 1933

Under the prevailing system of alternate wheat and summer-fallow farming in the semiarid area of eastern Washington and other similar areas, both the stubble and straw are commonly left in the field. The extremely wide nitrogen-carbon ratio of this residue results in reduced yields of the succeeding crop, and therefore burning it in the field is customary previous to plowing for summer-fallow. Such a practice is conducive to rapid depletion of soil nitrogen and organic matter, which might be maintained or even increased if the straw residue could be used effectively in promoting non-symbiotic aerobic nitrogen fixation sufficiently to establish a more favorable nitrogen-carbon ratio during the process of decomposition. Inasmuch as moisture and temperature conditions in summer-fallowed soil are generally very favorable for microbial activity, it is of special interest to procure more definite information regarding the activity of Azotobacter and the effect of additions of carbonaceous organic residues upon their nitrogen fixing power in soils on which the production of wheat or other cereals is alternated with summer-fallow. The work here presented was designed chiefly to study the activity of these organisms and its relationship to that of other important groups of microbes in soils of different reactions and organic matter content to which additional supplies of carbonaceous organic material had been added.

METHODS OF PROCEDURE

A preliminary experiment was carried on to compare the nitrogen fixing power and activity of Azotobacter in a manured soil with that in a non-manured soil both of which had been used in a previous investigation (11). The amount of nitrogen fixed in these soils, both with and without applications of carbonaceous organic residue, was determined by analysis for total nitrogen at the beginning and the end of the experiment. The activity of Azotobacter was estimated at intervals by plating definite amounts of soil on silica gel plates, according to the method of Winogradsky (15). A more detailed study of the

[1] Published as Scientific Paper No. 272, College of Agriculture and Agricultural Experiment Station, State College of Washington.

[2] Professor of soils and research assistant respectively.

...AD AGRIC...

comparative activity of Azotobacter and several other groups of soil microbes in relation to the reaction and the nitrogen and organic matter content of variously treated soils was made subsequently. The numbers of bacteria, fungi, Azotobacter, and cellulose decomposing bacteria were determined as separate groups at frequent intervals, and periodical analyses were made for carbon dioxide, organic carbon, nitrate nitrogen, and total nitrogen. The experiments were conducted at room temperature which varied between 20° and 25° C.

Preparations of soil samples.—Soil samples representing the surface 8 inches of Palouse silt loam were obtained from two of a series of field plots used for soil experimental work during the previous 27 years, and from a 6-acre area of virgin soil covered with native grass vegetation which had never been disturbed by plowing or harvesting. One of the field plots had been cropped with winter wheat every year and had received an annual fall application of farm manure at the rate of 12 tons per acre. The other plot had been in wheat in odd years and in summer-fallow in even years and had received no other residue than the wheat stubble. Because of scarcity of rainfall during the growing season, the fields in cereal crops in this area usually are dried out to a depth of several feet for a period of two or three months in summer. Therefore, the soil samples were obtained late in October following the harvest of the wheat and after the first fall rains had thoroughly moistened the surface layer 10 to 12 inches deep. The moist soil was spread evenly on paper in the laboratory, allowed to dry at room temperature until it could be handled freely without danger of puddling, and passed several times through a 6-mesh screen to obtain a uniform mixture of the soil and to eliminate coarse roots and other coarse organic material. Portions equivalent to 1,500 gm. of dry soil were used for each experiment, and water was added until the moisture content and consistency of the soil were similar to those in the field when it is in the best condition for tillage operations. Under these conditions, which have proved to be very satisfactory for this work, the normal moisture capacity of the soil as expressed by Shaw (8) is closely approached. By the addition of water when necessary, this moisture content was maintained within narrow limits throughout the experiments.

Finely ground filter paper passed through a 60-mesh sieve was used as organic residue, and a sufficient amount of sodium nitrate was added to make the nitrogen content of the paper equivalent to 2.5 per cent. The amount of readily available nitrogen thus provided is in accordance with the findings of Sievers and Holtz (9), who estimated that organic residues applied to Palouse silt loam should contain from 2.25 to 2.50 per cent nitrogen to overcome the well-known temporary depression in accumulation of nitrate nitrogen following the addition of carbonaceous materials that are low in nitrogen. In the first two experiments 1 per cent calcium carbonate as well as filter paper was added to the soil to prevent the possible occurrence of restricted Azotobacter activity which is often ascribed to lime deficiency. The soil samples were thoroughly

mixed with the ingredients first by hand and finally by several passages through a 6-mesh screen before they were put into wide-mouth bottles in which they were packed by gently tapping the bottles on the table. The bottles were connected with an absorption train for carbon dioxide determinations.

Samplings for soil analysis.—Several cores, representing the full depth of the soil were obtained with a butter sampler from each bottle and thoroughly mixed. The amount of the sample required for analysis was weighed, and the excess returned to the bottles, which were shaken and gently tapped on the table to fill the holes made by the sampler and to pack the soil properly. Unless otherwise stated, samplings were made on the first and second day after the experiment was started and every two days for a week thereafter. Following this time the interval between samplings was gradually increased until it was seven days, beginning with the second or third week. The samples intended for microbial analysis were spread very thinly on clean paper and air dried at laboratory temperature immediately following sampling. In this manner air-dry soil was obtained in 30 to 45 minutes with a minimum delay in the determination of the various groups of organisms.

Microbial analysis.—Conn's (3) direct microscopic technic with minor modifications was adopted for determining the number of bacteria in the soil. The 0.015 per cent gelatin recommended by Conn for the preparation of the soil suspension was substituted by 0.1 per cent agar, and *erythrosin*, instead of *rose bengal*, was used as a staining fluid.

The number of fungi was determined from soil suspensions by the dilution plate method, using potato extract agar adjusted to pH 3.2 to 3.4 by addition of sterilized 0.1 *N* citric acid previous to preparing the petri plates. Duplicate plates were prepared for each dilution, and the numbers recorded were computed from average counts of duplicate plates.

The Azotobacter and the cellulose decomposing bacteria were grown on silica gel plates 15 cm. in diameter. Winogradsky's (14) nutrient solution was used for the Azotobacter plates, and Waksman's (12) nutrient solution in addition to a sheet of filter paper superimposed upon the silica gel served as a medium for the growth of cellulose decomposing bacteria. Duplicate plates were prepared, one receiving twice as much soil as the other. The air-dried, pulverized soil was spread evenly over the entire surface of the gel in the plate at rates varying between 100 and 500 mgm., the exact amount in each case being determined arbitrarily on the basis of the number of organisms present in the soil at the previous sampling. Average counts of duplicate plates served as a basis for calculating the number of organisms per gram of dry soil.

Chemical analysis.—Total nitrogen and nitrate nitrogen were determined by the Kjeldahl and phenol-disulfonic acid procedures respectively, according to the official and tentative methods of analysis (1). The carbon dioxide was determined according to the method proposed by Heck (7), and the total carbon by the wet combustion method of Friedemann and Kendall (5). The

pH values were obtained by means of the quinhydrone electrode in suspensions of one part of soil to five parts of water.

TABLE 1

*Nitrogen fixing power of unmanured and manured Palouse silt loam treated with lime and with or without 1 per cent filter paper**

DAY OF SAMPLING	N FIXED BY THE AZOTOBACTER IN 10 DAYS IN 500 MGM. AIR-DRY SOIL ON SILICA GEL PLATES			
	Unmanured soil		Manured soil	
	Lime + filter paper	Lime	Lime + filter paper	Lime
	mgm.	*mgm.*	*mgm.*	*mgm.*
1	2.52	1.26	12.04	9.52
2	3.36	1.54	8.68	8.96
3	2.80	0.28	7.84	9.24
4	2.52	0.84	6.58	9.10
5	1.82	2.38	10.36	7.28
6	2.52	3.78	7.70	8.96
7	2.88	1.12	9.52	9.24
8	1.96	1.68	9.52	8.68
10	1.84	1.26	8.68	7.84
12	1.64	1.12	7.28	8.84
14	1.96	2.12	7.92	7.42
17	2.10	1.96	8.96	9.24
20	2.26	2.10	7.84	8.52
24	1.96	1.84	9.32	8.96
27	1.84	1.26	8.84	7.28
31	2.38	1.82	8.96	8.68
34	1.92	1.96	9.52	9.10
38	0.70	0.56	9.96	9.52
45	1.26	1.12	8.84	8.26
52	1.54	1.68	9.10	7.70
66	0.96	0.84	8.96	9.24
73	1.12	1.64	9.52	8.84
80	1.96	1.82	8.68	9.26
87	1.88	1.12	7.70	8.84
94	1.26	0.98	9.32	8.52
101	1.16	0.84	8.16	7.96
108	0.96	1.36	9.12	8.84
115	1.12	1.14	8.76	8.18
Average.....	1.86	1.48	8.85	8.64

* $NaNO_3$ added to make the nitrogen content of the filter paper equivalent to 2.5 per cent.

EXPERIMENTAL RESULTS

The chief purpose of the preliminary experiment was to determine whether fixation of atmospheric nitrogen in amounts capable of measurement by analytical methods occurs in Palouse silt loam and whether a marked variation in the organic matter content of the soil results in any appreciable difference

in the amount of nitrogen fixed by Azotobacter. The data obtained when duplicate 1,500-gm. portions of the unmanured and manured samples were treated with calcium carbonate and further handled as outlined in the methods of procedure for this experiment are recorded in tables 1 and 2.

The results show clearly that there was a striking difference in both the activity of Azotobacter and the quantities of nitrogen fixed in the two soils. The activity of Azotobacter, as shown by the average values of nitrogen recovered from the silica gel plates, was approximately five times as great in the manured as in the unmanured soil, and the difference in the total amounts of nitrogen fixed in these two soils at the end of the experiment was even more outstanding. The gain in total nitrogen in the manured soil was remarkably large considering the relatively short period (115 days) in which this took place. Similar increases in nitrogen have been reported, however, by Emmert

TABLE 2

Nitrate nitrogen and total nitrogen of variously treated unmanured and manured Palouse silt loam at the beginning and at the end of the experiment

SOIL AND TREATMENT	BEGINNING OF EXPERIMENT			END OF EXPERIMENT		N FIXED, BASED ON 2,000,000 LBS. DRY SOIL
	pH	N as NO_3	Total N	N as NO_3	Total N	
		p.p.m.	*per cent*	*p.p.m.*	*per cent*	*lbs.*
Unmanured:						
Lime	6.9	5.4	0.1411	36.0	0.1442	62
Lime + filter paper*	6.9		0.1661	76.0	0.1679	36
Manured:						
Lime	7.0	17.5	0.2257	64.5	0.2604	694
Lime + filter paper*	7.0		0.2507	108.0	0.2978	942

* $NaNO_3$ added to make the nitrogen content of the filter paper equivalent to 2.5 per cent.

(4) under greenhouse conditions in soils supplied with large quantities of manure, and by Wilsdon and Ali (13) under field conditions in an arid to semiarid climate in soils poorly supplied with organic matter. The data in table 1 indicate that the activity of Azotobacter was stimulated when 1 per cent filter paper was added, and in table 2 it is shown also that the addition of filter paper to the manured soil resulted in increased amounts of fixed nitrogen, suggesting that fresh carbonaceous organic residue as well as the organic matter content of the soil has a direct or indirect influence upon the activity of Azotobacter.

In an attempt to gain more information relative to the effect of the soil organic matter content and of additions of organic residue on the activity of Azotobacter, the experiment was repeated with fresh samples, using essentially the same soil treatments but substituting for the unmanured soil a virgin soil in which the organic matter was derived entirely from the native grass vegeta-

tion, and intermediate in amount between that of the manured and unmanured soils. The method of procedure in this experiment was modified considerably. Instead of measuring the nitrogen fixing power of Azotobacter by spreading small quantities of soil on silica gel plates, the number of these organisms was determined. The total microbial activity and the comparative activity of the bacteria, fungi, and cellulose decomposing bacteria in relation to the activity of Azotobacter and as affected by soil organic matter and additions of carbonaceous organic residue were also determined. This was done at the intervals

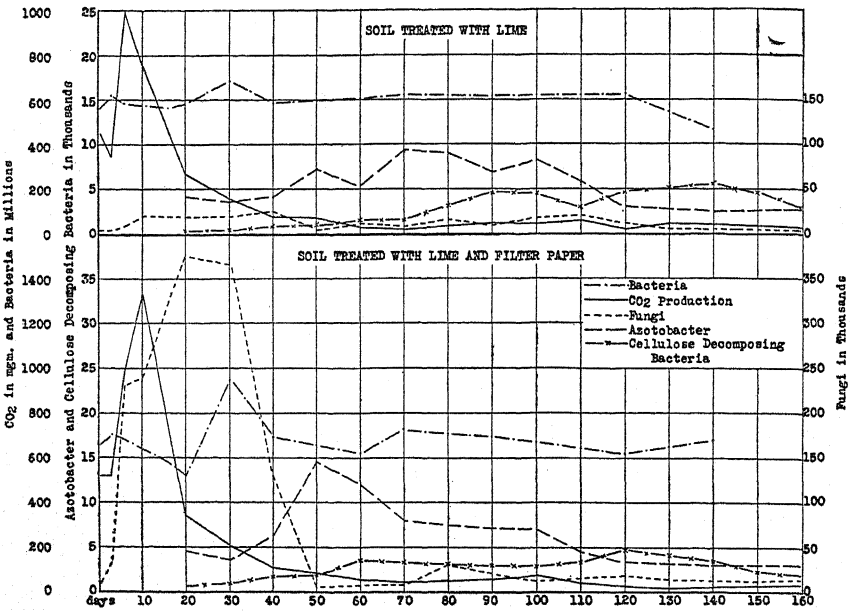


FIG. 1. MICROBIAL DEVELOPMENT AND CO_2 PRODUCTION IN MANURED PALOUSE SILT LOAM

Microbes given in numbers per gram and CO_2 in milligrams per 100 gm. of dry soil based on average values of determinations between 10-day intervals following first 10-day period. $NaNO_3$ added to make N content of filter paper equivalent to 2.5 per cent.

by the methods already described. The results are given in figures 1 and 2 and in tables 3 and 4.

Observations made while the work was in progress indicated that the reduction or increase in numbers of organisms of a specific group of microbes had a tendency to follow a somewhat gradual course, except for the first few days when marked changes in microbial activity occurred rapidly following the application of large amounts of fresh organic residue or the addition of the proper amount of moisture to air-dry soil. Therefore, the trend of changes taking place in the activity of these groups is represented in figures 1 and 2 as average values of two or three samplings during the first 10 days of the ex-

periment and as average values of the determinations made within periods of 10 days following that time.

Although the most intensive evolution of carbon dioxide occurred during the first 10 days, irrespective of soil or treatment, this activity was greatly stimulated by the addition of filter paper, which, however, was more effective in the virgin than in the manured soil. Following the initial 10-day period, the evolution of carbon dioxide proceeded at a low rate in all soils.

The maximum numbers of bacteria and fungi, which were the first to show increased activity, did not appear until several days after the peak in carbon

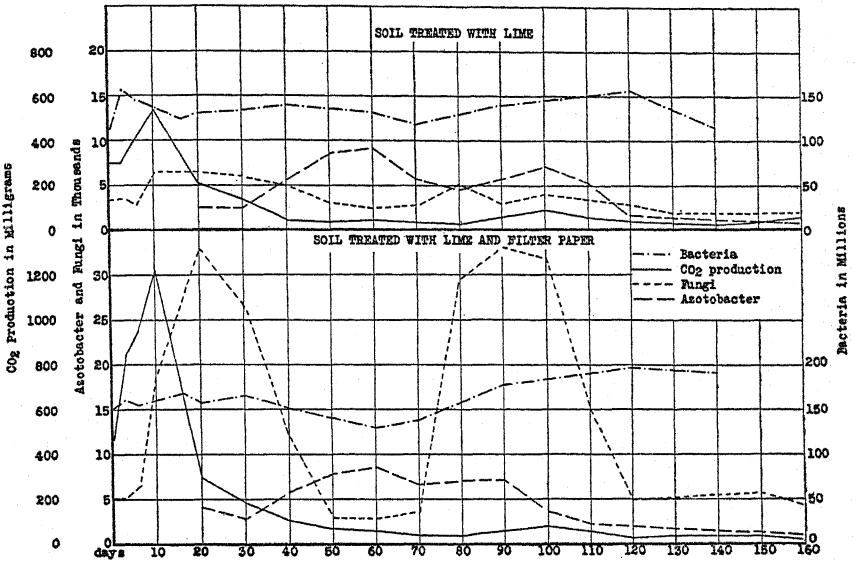


FIG. 2. MICROBIAL DEVELOPMENT AND CO_2 PRODUCTION IN VIRGIN PALOUSE SILT LOAM

Microbes given in numbers per gram and CO_2 in milligrams per 100 gm. of dry soil based on average values of determinations between 10-day intervals following first 10-day period. $NaNO_3$ added to make N content of filter paper equivalent to 2.5 per cent.

dioxide evolution had been reached. Thus, the activity of these organisms as shown by carbon dioxide evolution did not coincide with the increase in numbers of organisms, indicating that numbers alone are not necessarily an accurate index of the activity of soil microbes. The fact that bacteria and, especially, fungi were the first to take advantage of the available food supply suggests that they successfully competed with other groups of microbes in utilizing the readily available organic compounds. The fungi seemed to be more selective in their food requirements than the bacteria, as they responded quickly to the additions of organic residue, and the relative fluctuation in their numbers was much greater than in the numbers of bacteria, which remained

relatively uniform throughout the experiment. Although the activity of fungi was somewhat greater in the virgin than in the manured soils, the second

TABLE 3

Nitrate nitrogen and total nitrogen of variously treated virgin and manured Palouse silt loam at the beginning, at 80 days, and at the end of the experiment

SOIL AND TREATMENT	BEGINNING OF EXPERIMENT			80 DAYS		END OF EXPERIMENT		N FIXED, BASED ON 2,000,000 LBS. DRY SOIL AT END OF EXPERIMENT
	pH	N	N as NO_3	N	N as NO_3	N	N as NO_3	
		per cent	*p.p.m.*	*per cent*	*p.p.m.*	*per cent*	*p.p.m.*	*lbs.*
Virgin:								
Lime	6.9	0.2160	Trace	0.2255	9.6	0.2268	36.5	216
Lime + filter paper*	7.0	0.2410		0.2673	17.0	0.2687	94.0	554
Manured:								
Lime	7.0	0.2257	17.5	0.2716	19.4	0.2690	46.5	866
Lime + filter paper*	7.1	0.2507		0.2929	26.2	0.3039	154.0	1,064

* $NaNO_3$ added to make the nitrogen content of the filter paper equivalent to 2.5 per cent.

TABLE 4

Relation of nitrogen fixed to nitrogen and organic matter content of variously treated Palouse silt loam

SOIL AND TREATMENT	BEGINNING OF EXPERIMENT			END OF EXPERIMENT			N FIXED, BASED ON 2,000,000 LBS. DRY SOIL	
	N	C	N:C	N	C	N:C	Expt. 1	Expt. 2
	per cent	*per cent*		*per cent*	*per cent.*		*lbs.*	*lbs.*
Unmanured:								
Lime	0.1411	1.47	10.4	0.1442	1.41	9.8	62	...
Lime + filter paper*	0.1661	1.69	10.2	0.1679	1.52	9.1	36	...
Manured:								
Lime	0.2257	2.87	12.7	0.2604	2.83	10.5	694	...
Lime + filter paper*	0.2507	3.42	13.6	0.2978	3.11	10.4	942	...
Virgin:								
Lime	0.2160	2.25	10.4	0.2268	2.37	10.4	...	216
Lime + filter paper*	0.2410	2.48	10.3	0.2687	2.55	9.5	...	554
Manured:								
Lime	0.2257	2.87	12.7	0.2690	2.59	9.6	...	866
Lime filter paper*	0.2507	3.42	13.6	0.3039	3.34	11.0	...	1,064

* $NaNO_3$ added to make the nitrogen content of the filter paper equivalent to 2.5 per cent.

sudden rise in their number, occurring in the third month in the virgin soil treated with filter paper, can not be explained on the basis of the results obtained from the other soils.

The enumeration of Azotobacter and cellulose decomposing bacteria was not begun until the twentieth day, but judging from the trend of the curves it seems safe to assume that during the first month of the experiment their activity was not materially affected by any of the treatments. Following this period, and continuing for about 11 weeks, there was a marked increase in numbers of Azotobacter regardless of soil treatment, and after that time the numbers dropped to a low level in all cases. The increase in numbers following the first month corresponded closely with a decided stimulation in nitrogen fixation, for it was undoubtedly during this period that the greatest part of the gain in the total nitrogen was obtained, as can be noted from the data in table 3. However, the curves in figures 1 and 2 do not show that the activity of Azotobacter was materially affected by the addition of carbonaceous organic residue, whereas the data in table 3 and also in table 2 show clearly that the nitrogen fixation in the soils was greatly stimulated as a result of this treatment.

A possible symbiosis of Azotobacter with cellulose decomposing bacteria has been suggested by various investigators. The curves in figure 1 show that the numbers of cellulose decomposing bacteria were comparatively small and that their increased development began later but also subsided later than the increased activity of Azotobacter. They were relatively inactive at all times in the virgin soils, as their numbers seldom exceeded 150 colonies per gram of dry soil, and for that reason could not be shown conveniently in figure 2.

It would appear that on account of the relatively small numbers of the cellulose decomposing bacteria their activity did not have any significant bearing upon the activity and nitrogen fixing power of Azotobacter.

In considering the relationship of these various groups of microbes, it is obvious that in the presence of some available nitrogen the fungi and probably the bacteria also are quick in making use of the readily available organic compounds either originally present in the soil or supplied in the form of carbonaceous organic material. Supposedly the majority of these compounds are likewise an excellent source of energy for Azotobacter, but apparently they could not be used by this group as long as the fungi were in the competitive field. It is significant that the activity of Azotobacter became most intensive after this readily available food supply was exhausted and probably at a time when soluble nitrogen other than that supplied in the form of nitrate was in the process of accumulation, since it is well known that supplies of soluble nitrogen such as were added to the filter paper are used up in a few days when the microbial activity in the soil is optimum. It would seem, therefore, that the Azotobacter group thrives on compounds that are not readily available for fungi or possibly on dead cellular tissue of fungi and other microbes.

Winogradsky (16) and Ziemiecka (17) concluded, from their work on soils from experimental plots treated with various fertilizers over a period of years, that the addition of nitrogen fertilizers to the soil causes a reduction in the activity of Azotobacter presumably on account of the presence of available nitrogen. The data in table 3 show that nitrogen fixation was most active in

those soil samples that had received available nitrogen and that, at the time when nitrogen fixation was still active, contained larger amounts of nitrate nitrogen than were added annually to the field plots studied by the authors mentioned. The data in table 4 further indicate that the largest increase in total nitrogen occurred in the soil that was best supplied with organic matter and that the amounts fixed in the other soils were somewhat proportional to their organic matter contents. Apparently the quantities of soluble nitrogen that ordinarily accumulate in the soil under field conditions do not necessarily interfere appreciably with the normal functions of Azotobacter, provided the proper kind and amount of organic food supply are available. The nitrogen-carbon ratio of the soils did not seem to affect the functions of Azotobacter, as this ratio was approximately the same for the unmanured and virgin soils, whereas the nitrogen fixing power in these soils varied greatly.

The large gain in total nitrogen obtained in this experiment might appear to be unusual were it not for the fact that the manured soil, which was also used in the preliminary experiment and received identical treatments, gave strikingly similar results. It is significant that by far the largest part of the increase in total nitrogen was accumulated during the short time in which the Azotobacter group was very active and under conditions of moisture and aeration that were unfavorable for anaerobic organisms. At the same time, it should be noted that in three of the four samples receiving filter paper the process of nitrogen fixation was favored decidedly by the addition of fresh carbonaceous organic residue, although the activity of Azotobacter as shown by numbers present did not appear to be affected correspondingly. Possibly the observed increase in nitrogen cannot be fully accounted for by the activity of the Azotobacter group. Carter and Greaves (2) and Greaves and Greaves (6) have isolated a number of actinomyces and bacteria that seem to be capable of fixing small amounts of atmospheric nitrogen. This phase of the problem is worthy of further investigation. It is possible also that the remarkable fixation observed in this experiment would rarely, if ever, occur under field conditions or might not be reproduced in the laboratory if the soil samples were obtained from the field at a different time of the year. In previous work in this laboratory (10) it was shown that the number of active Azotobacter fluctuates greatly during different seasons of the year. That the activity of these organisms in the field may also vary from year to year was demonstrated by the work of Wilsdon and Ali (13), who found large increases in total nitrogen in certain soils during one year and no appreciable gains during the three following years. The activity of the Azotobacter group under field conditions seems to be erratic, and much additional work will be required to understand properly its relationship to different soil and environmental conditions.

The results of the two experiments with Palouse silt loam show conclusively that non-symbiotic aerobic nitrogen fixation was stimulated when large quantities of carbonaceous organic material were applied to those soils that were best supplied with organic matter and, furthermore, the data are strongly

suggestive that in the utilization of fresh carbonaceous organic residue there is a sequence of activity of important groups of microbes which definitely affects the process of non-symbiotic aerobic nitrogen fixation. Should these observations be borne out by future studies, the huge quantities of straw residue now commonly destroyed by fire in the wheat fields of semiarid areas could be returned to the soil profitably, since this residue could be made to serve not only as a valuable source of energy for the process of atmospheric nitrogen fixation, but also as an indispensable foundation for the maintenance of the rapidly disappearing soil organic matter. Further work on this problem is in progress and will be reported in a subsequent paper.

EFFECT OF SOIL REACTION ON MICROBIAL ACTIVITY

The extraordinary response in development of fungi, following the addition of filter paper to soils of neutral reaction which is generally presumed not to be favorable for the growth of fungi, suggests that the food supply may be a more important factor in the activity of these and other soil microbes than has been suspected heretofore. In order to study the effect of soil reaction on the total microbial activity and on the activity of specific groups of microbes, three portions each equivalent to 1,500 gm. of dry soil of the manured and unmanured samples respectively were adjusted to different reactions. On account of the high buffer capacity of Palouse silt loam, large quantities of acid or basic substances were required to bring about the desired changes in hydrogen-ion concentration. Since the addition of a large quantity of a single acid, such as sulfuric acid, for example, may have specific effects other than its effect on reaction, a mixture of equivalent parts of sulfuric, citric, and hydrochloric acids was used to overcome this difficulty, at least partially. Calcium carbonate was used as basic material to obtain the desired alkalinity of the alkaline soils.

The reaction of the acid samples was adjusted to a value of pH 5.5, that of the alkaline samples to a value of pH 8.1, and that of the two remaining samples was kept at the original hydrogen-ion concentration of pH 7.0. These values were maintained in the moist samples for 8 days before the 1 per cent finely ground filter paper treated with sodium nitrate as described in the methods of procedure was applied. The microbial activity was then determined in the same manner as in the previous experiment, except that the interval between samplings was 5 days for the first 3 weeks, and 10 days for the remaining period.

There was no appreciable change in reaction of the soils 3 weeks after the experiment was in progress, but, as can be seen from the data in table 5, a considerable change in pH value had occurred in the acid and alkaline samples at the end of the experiment. The change in both the acid and alkaline samples had proceeded in the direction of neutrality, probably a result of the buffer effect of the soils and not of the microbial activity.

The total microbial activity as shown by the carbon dioxide curves in figure

3 was slightly greater in the acid than in the neutral or alkaline soils during the first 10 days, but after that time it was very similar in all soils. The data in table 5 show also that the total amounts of carbon dioxide liberated from the soils during the 3 months in which the experiment was in progress were greatest in the acid soils. The differences may not be significant, as the organic acid, which was added to bring about the desired acidity, probably supplied sufficient readily available food to account for the apparent increased liberation of carbon dioxide.

The activity of the bacteria as indicated in figure 3 was comparatively uniform in all soils regardless of hydrogen-ion concentration. The activity of the Azotobacter and cellulose decomposing bacteria, as shown in the same figure, varied somewhat in the different soil samples; but these variations were not consistent and, therefore, cannot be considered significant. The activity of fungi, however, was markedly affected by soil reactions.

TABLE 5

*Moisture content, pH value, and CO_2 production in unmanured and manured Palouse silt loam adjusted to distinctly acid, neutral, and alkaline reactions and treated with 1 per cent filter paper**

	UNMANURED SAMPLES			MANURED SAMPLES		
	1	2	3	1	2	3
Per cent moisture at beginning	19.50	19.50	19.50	22.00	22.00	22.00
Per cent moisture at end	19.50	19.30	19.50	22.00	21.00	22.00
pH at beginning	5.5	8.1	6.9	5.5	8.1	7.0
pH at end	6.1	8.2	6.9	6.3	7.8	7.2
Total CO_2 in gm. evolved from 100 gm. of soil	1.51	1.33	1.24	1.46	1.42	1.37

* $NaNO_3$ added to make the nitrogen content of the filter paper equivalent to 2.5 per cent.

The effect of alkalinity on the development of fungi in the soil adjusted to a value of pH 8.1 is obvious, as the numbers were much smaller than in either the neutral or acid soils. This may have an important bearing upon the microbial activity of soils of arid regions where distinctly alkaline or alkali soils prevail, but is applicable only in exceptional cases in soils of the humid regions. In this connection it is significant to note that the activity of this group of microbes in the distinctly acid soils with a pH value of 5.5 did not vary greatly from that in the neutral soils with a pH of 7.0. Perhaps a more acid reaction than pH 5.5 might have been more favorable for the fungus group, but that is not so important from the practical standpoint, as the range of hydrogen-ion concentrations of the majority of soils under cultivation falls within the extreme pH values covered by this experiment. It might be expected also that other soils with the same reactions as the ones used in this experiment, but with different inherent characteristics, would give different results.

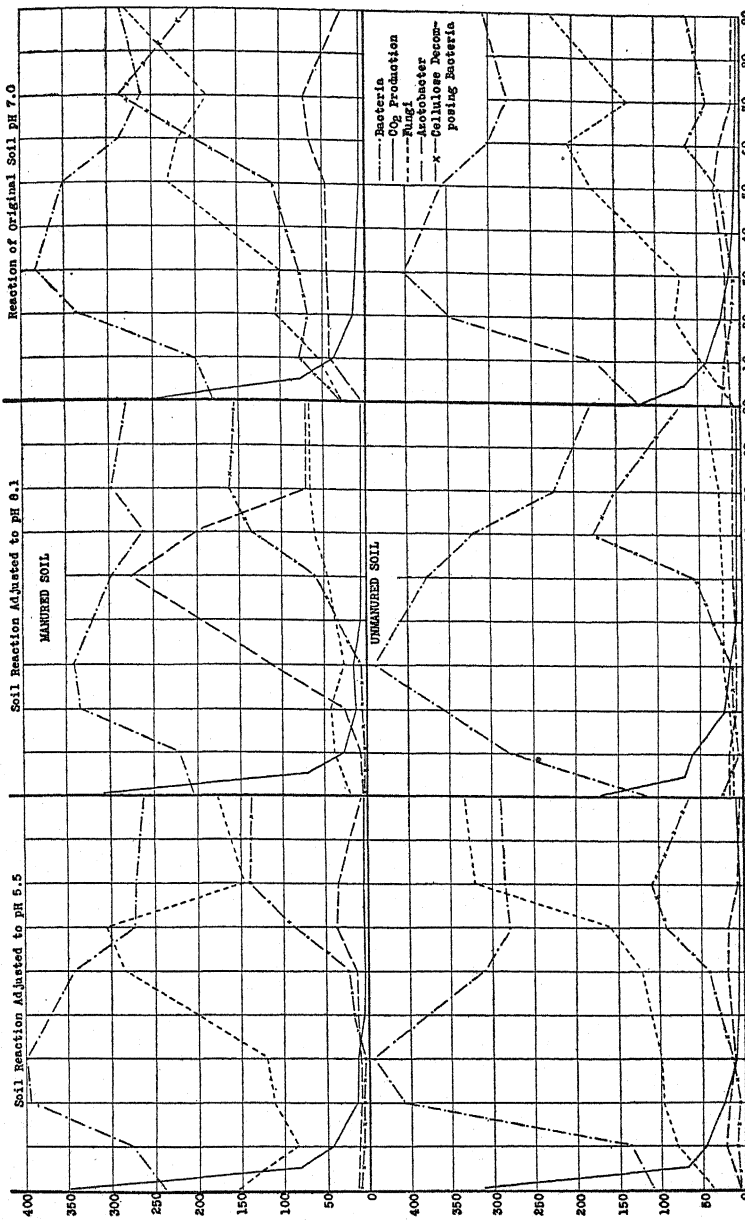


FIG. 3. MICROBIAL DEVELOPMENT AND CO_2 PRODUCTION IN MANURED AND UNMANURED PALOUSE SILT LOAM AT DIFFERENT pH VALUES

Microbes given in numbers per gram and CO_2 in milligrams per 100 gm. of dry soil based on average values of determinations between 10-day intervals.

The significant point brought out by these data is that the activity and development of several important groups of microbes proceeded normally under a relatively wide range of hydrogen-ion concentrations in the soil. It seems, therefore, that the hydrogen-ion concentration as such, provided it is within the limits occurring in the large majority of cultivated soils, does not affect the normal activity of the general soil microflora so much as does the available food supply.

SUMMARY

Nitrogen fixation in three different Palouse silt loam soils treated with lime and carbonaceous organic residue was determined in 1,500-gm. samples in the laboratory. A study was also made of the comparative activity of Azotobacter, total bacteria, fungi, and cellulose decomposing bacteria in these soils as affected by added carbonaceous organic material, reaction, and nitrogen and organic matter content.

The quantities of nitrogen fixed during the course of the experiment varied with the organic matter content of the soils. On the basis of 2,000,000 pounds of dry soil the gain in total nitrogen ranged from 36 pounds for the soil with an original organic carbon content of 1.47 per cent to 1,064 pounds for the soil with an original organic carbon content of 2.87 per cent. Nitrogen fixation was greatly stimulated in three of the four soil samples which had received large amounts of carbonaceous organic residue.

The total nitrogen content of the soil, the nitrogen-carbon ratio of the organic matter, or the comparatively large quantities of nitrate nitrogen present in the soils while atmospheric nitrogen fixation was in progress, did not seem to affect the activity of Azotobacter to any appreciable extent.

In the presence of available nitrogen, the fungi and bacteria were first to make use of the readily available organic compounds either originally present in the soil or supplied by additions of carbonaceous organic material. The activity of Azotobacter became most intensive after this readily available supply of organic compounds was exhausted, and apparently these organisms were capable of utilizing compounds that are not readily available for fungi.

The activity of cellulose decomposing bacteria was comparatively small and did not seem to have any significant bearing upon the activity of Azotobacter.

The transformation of organic residue was associated with a distinct sequence in development of important groups of soil microbes through which the process of non-symbiotic aerobic nitrogen fixation appeared to be directly affected.

The activity of bacteria, Azotobacter, and cellulose decomposing bacteria was not materially affected by soil reactions ranging between the pH values of 5.5 to 8.1, whereas the development of fungi was greatly retarded when the hydrogen-ion concentration was at pH 8.1 and slightly favored when it was at pH 5.5.

The apparently normal activity of these important groups of soil microbes in a wide range of soil reactions suggests that the available food supply and

possibly also the nature of the inherent soil characteristics are more potent factors in the activity of the soil microflora than is soil reaction, provided this reaction is within the limits generally occurring in the large majority of cultivated soils.

REFERENCES

(1) Association of Official Agricultural Chemists 1930 Official and Tentative Methods of Analysis, ed. 3, p. 5–405. Washington, D. C.

(2) CARTER, E. G., AND GREAVES, J. D. 1928 The nitrogen fixing microörganisms of an arid soil. *Soil Sci.* 26: 179–191.

(3) CONN, H. J. 1929 Use of the microscope in studying the activities of bacteria in soil. *Jour. Bact.* 17: 399–405.

(4) EMMERT, E. M. 1931 The effect of soil reaction on the growth of tomatoes and lettuce and on the nitrogen, phosphorus, and manganese content of the soil and plant. Ky. Agr. Exp. Sta. Res. Bul. 314.

(5) FRIEDEMANN, T. C., AND KENDALL, A. I. 1929 The determination of carbon and carbon dioxide. *Jour. Biol. Chem.* 82: 45–55.

(6) GREAVES, J. E., AND GREAVES, J. D. 1932 Nitrogen fixers of leached alkali soils. *Soil Sci.* 34: 375–383.

(7) HECK, A. F. 1929 A method for the determination of total carbon and also the estimation of carbon dioxide evolved by soils. *Soil Sci.* 28: 225–255.

(8) SHAW, C. F. 1927 The normal moisture capacity of soils. *Soil Sci.* 23: 303–317.

(9) SIEVERS, F. J., AND HOLTZ, H. F. 1922 The silt loam soils of eastern Washington and their management. Wash. Agr. Expt. Sta. Bul. 166.

(10) VANDECAVEYE, S. C., AND ANDERSON, S. 1933 Longevity of Azotobacter in soils treated with lime and superphosphate. *Jour. Amer. Soc. Agron.* 26: 353–364.

(11) VANDECAVEYE, S. C., AND VILLANUEVA, B. R. 1934 Morphological relationships of soil microbes. *Jour. Bact.* 27: 257–269.

(12) WAKSMAN, S. A., AND CAREY, C. 1926 The use of the silica gel plate for demonstrating the occurrence and abundance of cellulose decomposing bacteria. *Jour. Bact.* 12: 87–95.

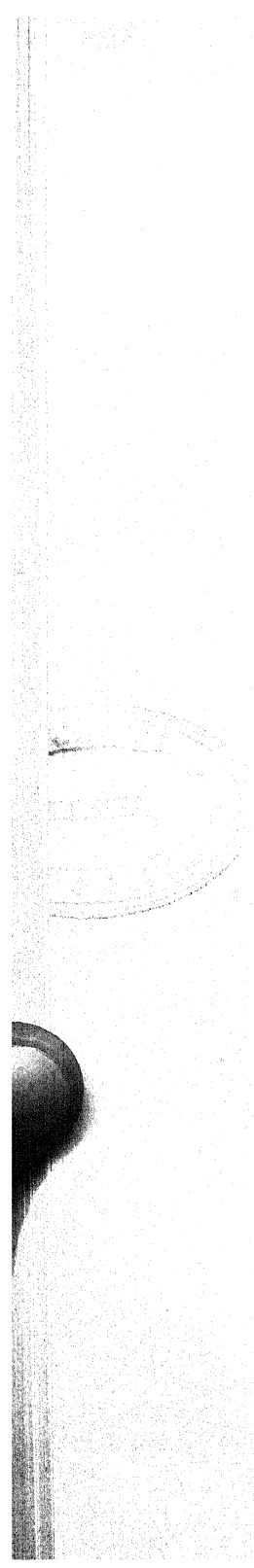
(13) WILSDON, B. H., AND ALI, B. 1922 Nitrogen fixation in arid climates. *Soil Sci.* 14: 127–133.

(14) WINOGRADSKY, S. 1925 Études sur la microbiologie du sol: I. Sur la méthode. *Ann. Inst. Pasteur* 39: 299–354.

(15) WINOGRADSKY, S. 1926 Études sur la microbiologie du sol: II. Sur les microbes fixateurs d'azote. *Ann. Inst. Pasteur* 40: 455–520.

(16) WINOGRADSKY, S. (in collaboration with Ziemiecka, J.) 1928 Études sur la microbiologie du sol: III. Sur le pouvoir fixateur des terres. *Ann. Inst. Pasteur* 42: 36–62.

(17) ZIEMIECKA, J. 1932 The Azotobacter test of soil fertility applied to the classical fields at Rothamsted. *Jour. Agr. Sci.* 22: 797–810.



PHYSIOLOGICAL STUDIES ON RHIZOBIUM: II. THE EFFECT OF NITROGEN SOURCE ON OXYGEN CONSUMPTION BY RH. MELILOTI, RH. TRIFOLII, AND RH. PHASEOLI[1]

R. H. WALKER, D. A. ANDERSON, AND P. E. BROWN

Iowa Agricultural Experiment Station

Received for publication September 15, 1933

In the first paper of this series (1), data were presented showing the effects of nitrogen source on oxygen consumption by *Rhizobium leguminosarum*. In that work it was shown that in the absence of combined nitrogen there was no stimulation of growth, and that the cells continued to respire at a slightly decreasing rate throughout the duration of the tests. When yeast extract was added to the medium, there was a marked stimulation in the rate of oxygen consumption, the increase in rate being somewhat proportional to the amount of yeast extract added. After a certain period, usually about 12 hours, the rate of oxygen consumption became practically uniform, and presumably the cells, at that time, had passed their logarithmic phase of growth and from then on were in a resting state, but they continued to respire. When other nitrogenous materials—ammonium chloride, sodium nitrate, urea, or alanine—were added to the medium instead of yeast extract, there was no marked stimulation of growth irrespective of the kind or amount added, within the limits of the experiment. There was some indication that the ammonium chloride and urea, in the highest concentrations, slightly depressed oxygen consumption. It is not definitely known whether it was the nitrogen or some other constituent of the yeast extract that was the active agent in stimulating oxygen consumption and growth.

In order to secure further information concerning the nitrogen nutrition and metabolism of this important and interesting genus of bacteria, further experiments, similar to those already conducted with *Rh. leguminosarum* have been planned in which the effects of the various nitrogen sources on the consumption of oxygen by other species of the genus have been investigated. In the work reported here, studies were made with *Rh. trifolii*, *Rh. meliloti*, and *Rh. phaseoli*, the root-nodule bacteria of red clover, alfalfa, and garden beans, respectively.

The organisms were grown in a medium to which no combined nitrogen was added and also in media containing nitrogen from different sources. The nitrogen sources employed in this work were bacto-yeast extract, ammonium

[1] Journal paper no. *J*-124 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 226.

chloride, sodium nitrate, urea, and alanine. To separate cultures, these materials were added in various amounts to give the following concentrations of nitrogen: 0.72, 7.2, 36.0, 72.0, and 144.0 p.p.m. of solution.

The oxygen consumed by the organisms in the various media was measured in respiration vessels and micromanometers of the type used by Warburg (2) in his studies on the metabolism of tumors. The details of the procedure and also the methods followed in preparing the inocula are described in a previous paper (1).

RESULTS

The results obtained in the studies with the different species under consideration are presented separately in the following.

TABLE 1

Oxygen consumption by Rhizobium trifolii in media containing yeast extract

TIME	NO NITROGEN	AMOUNTS OF NITROGEN AS YEAST EXTRACT IN MEDIA				
		0.72 p.p.m.	7.2 p.p.m.	36.0 p.p.m.	72.0 p.p.m.	144.0 p.p.m.
hrs.	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	8.6	12.6	14.8	19.8	19.1	19.0
4	20.9	30.5	36.0	45.3	45.6	43.4
5	33.2	45.4	52.3	63.7	73.7	62.0
6	35.0	47.6	60.1	76.4	76.2	73.8
8	44.0	57.3	80.9	76.2	116.4	110.5
10	52.6	66.2	101.4	146.4	170.9	167.6
12	54.2	68.1	112.7	173.7	224.1	241.0
14	61.0	75.5	129.7	216.2	288.4	339.7
16	69.0	84.4	148.8	259.4	358.2	443.4
18	74.0	90.3	162.9	302.6	425.2	546.6
20	83.5	102.9	183.0	379.8	501.3	656.3
22	92.8	112.9	199.6	428.6	576.8	762.2
24	100.0	121.8	215.2	476.4	651.3	863.8
26	108.0	132.5	232.9	525.2	724.8	959.2
28	114.4	140.7	245.9	568.4	797.0	1,046.8
30	120.8	149.2	260.7	609.4	876.5	1,130.0

Rhizobium trifolii.—The data obtained in the oxygen consumption experiments with *Rh. trifolii* when grown in media containing varying amounts of bacto-yeast-extract are shown in table 1. The data show that throughout the entire test the cells in the no-nitrogen medium continued to respire and consume oxygen. There may have been some slight growth and multiplication, by the organisms, during the first 3 or 4 hours after they were introduced into the medium. If there was any growth at that time it was undoubtedly induced by the small amount of nitrogen carried over in the inoculum. The exact amount of nitrogen introduced in this way was not known, but it is evident

that it was extremely small, as considerable care was taken in the preparation of the inoculum to have it as free of nitrogen as possible. After the fifth hour the rate of oxygen consumption was at a minimum, and it continued at this low point throughout the test period. Undoubtedly the cells were in a state of rest during that time, and there was no growth or multiplication.

In the medium containing 0.72 p.p.m. of yeast extract nitrogen there was some stimulation of growth in the early period, but it may be clearly seen that the increased rate of oxygen consumption did not continue long, presumably because the small amount of yeast extract in the medium was soon used by the organisms. After the period of stimulation, respiration and oxygen consumption continued at a fairly uniform rate similar to that in the medium

TABLE 2

Oxygen consumption by Rhizobium trifolii in media containing ammonium chloride

TIME	NO NITROGEN	AMOUNTS OF NITROGEN AS AMMONIUM CHLORIDE IN MEDIA				
		0.72 p.p.m.	7.2 p.p.m.	36.0 p.p.m.	72.0 p.p.m.	144.0 p.p.m.
hrs.	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	10.7	11.7	9.3	12.0	9.5	11.1
4	16.8	16.6	14.0	15.3	13.1	13.4
6	24.7	22.6	19.7	20.0	18.0	16.3
8	34.8	30.6	26.5	25.7	23.0	20.0
10	44.3	38.8	33.9	34.0	30.4	24.1
12	52.6	47.0	41.8	40.8	39.3	28.3
15	64.6	60.3	53.4	54.9	50.8	34.0
18	75.6	74.9	65.3	67.2	62.5	39.3
20	84.1	86.4	76.3	76.5	72.0	43.8
22	92.0	97.8	86.1	83.4	80.0	47.2
24	98.4	109.6	97.8	87.9	88.7	50.9
26	104.9	119.3	107.4	96.8	96.1	53.6
28	110.5	130.1	116.6	108.1	103.1	56.7
30	118.9	144.4	138.5	112.6	112.5	60.1

without nitrogen. The total amount of oxygen consumed by the organisms in the yeast extract medium during the test was higher than that consumed by the organisms in the medium without yeast extract. This was undoubtedly due to the slightly greater stimulation in the early part of the test.

In the media containing the larger amounts of yeast extract, there was also a stimulation of growth in the early part of the test. The larger the amount of yeast-extract in the medium the greater was the stimulation of growth and oxygen consumption. The increase in rate of oxygen consumption lasted for a period of about 14 hours, during which time the organisms were undoubtedly growing rapidly and they were, presumably, in the logarithmic phase of growth. After that period the rate of oxygen consumption remained nearly uniform, except for a few unaccountable variations, until the end of the test. During

this time the organisms probably had passed into the later phases of the growth cycle and presumably they were in a resting condition, but they continued to respire and consume oxygen.

TABLE 3

Oxygen consumption by Rhizobium trifolii in media containing sodium nitrate

TIME	NO NITROGEN	AMOUNTS OF NITROGEN AS SODIUM NITRATE IN MEDIA				
		0.72 p.p.m.	7.2 p.p.m.	36.0 p.p.m.	72.0 p.p.m.	144.0 p.p.m.
hrs.	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	2.7	3.7	1.8	7.8	3.5	7.1
4	4.6	5.9	4.6	11.3	6.3	9.1
6	7.1	8.4	6.7	15.5	8.4	11.1
8	11.8	12.0	9.9	20.2	12.3	14.9
10	15.4	15.9	14.0	26.4	17.0	18.8
12	21.0	19.5	17.0	31.5	19.9	22.1
14	27.4	23.5	22.7	37.2	25.5	27.8
16	33.0	27.5	26.5	43.1	30.4	32.6
18	37.7	31.7	30.5	48.0	33.9	35.2
20	42.9	37.2	36.2	56.1	39.8	41.7
22	47.8	42.4	40.7	62.5	44.3	46.0
24	51.7	48.1	45.6	68.4	49.2	50.1
26	56.6	54.0	51.3	76.2	54.8	55.5
28	61.0	58.2	54.5	83.0	59.1	58.4
30	66.1	64.0	60.7	92.0	66.2	64.6

TABLE 4

Oxygen consumption by Rhizobium trifolii in media containing urea

TIME	NO NITROGEN	AMOUNTS OF NITROGEN AS UREA IN MEDIA				
		0.72 p.p.m.	7.2 p.p.m.	36.0 p.p.m.	72.0 p.p.m.	144.0 p.p.m.
hrs.	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	7.6	8.0	9.6	9.2	3.5	8.8
4	13.0	11.9	13.6	12.5	7.8	14.0
6	18.1	17.1	18.7	17.3	12.7	18.2
9	26.9	27.5	27.3	25.2	20.7	25.9
12	36.8	40.1	37.6	36.5	31.9	37.0
15	43.0	49.0	46.1	45.0	40.3	45.2
18	54.7	62.2	62.4	59.9	55.4	59.2
21	64.6	71.1	78.7	75.5	73.1	74.4
23	70.5	80.2	91.4	84.0	77.7	79.2
26	78.9	90.3	106.7	98.6	92.4	90.5
28	83.5	96.2	117.6	109.2	102.2	97.3
30	88.7	101.7	130.3	119.0	110.9	104.5

In the media containing the other forms of nitrogen, ammonium chloride, sodium nitrate, urea, and alanine, there was no large stimulation of oxygen

consumption such as there was in the yeast extract media. This is shown by the data for the consumption of oxygen by *Rh. trifolii* in these media which are recorded in tables 2, 3, 4, and 5. The data indicate that small amounts of nitrogen as ammonium chloride probably stimulated oxygen consumption and growth to a very slight extent, but larger amounts seemed to be definitely depressive.

The nitrogen added as sodium nitrate seemed to have no effect on the rate or amount of oxygen consumed, irrespective of the amount added. The nitrogen added as urea probably was stimulative to a very limited extent, but the nitrogen as alanine was definitely stimulative, although the extent of the stimulation was not great in any case when compared with the stimulation

TABLE 5

Oxygen consumption by Rhizobium trifolii in media containing alanine

TIME	NO NITROGEN	AMOUNTS OF NITROGEN AS ALANINE IN MEDIA				
		0.72 p.p.m.	7.2 p.p.m.	36.0 p.p.m.	72.0 p.p.m.	144.0 p.p.m.
hrs.	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*	*c.mm.*
0	0.0	0.0	0.0	0.0	0.0	0.0
2	12.6	17.4	15.8	14.0	8.2	14.8
4	19.4	25.6	23.6	21.1	15.2	23.0
6	26.2	35.3	33.5	28.9	22.2	30.5
8	34.8	48.7	45.9	39.5	32.0	41.0
10	42.0	60.3	56.5	50.5	42.0	52.0
13	54.6	82.4	78.0	69.9	60.6	71.3
15	63.2	95.8	91.4	83.3	73.9	85.6
18	74.5	111.4	110.5	102.4	91.4	104.6
21	87.8	130.0	134.5	127.4	114.4	127.0
23	95.8	141.2	149.3	143.4	127.7	140.6
26	106.9	156.4	170.1	172.8	148.0	158.3
28	114.3	167.3	185.4	196.8	161.3	171.2
30	122.1	176.5	201.7	220.4	174.8	184.1

induced by the yeast extract. The comparative effects of the different forms of nitrogen on the consumption of oxygen by *Rh. trifolii* are shown in figure 1. The curves in this figure represent the ratios of the amounts of oxygen consumed by the organisms in the various media compared with the amount consumed in the medium without added nitrogen. It is shown that, in general, the respiration and growth of *Rh. trifolii* were affected in the same manner by the various forms of nitrogen as were the respiration and growth of *Rh. leguminosarum* which were considered in a previous paper (1).

Rhizobium meliloti.—The amounts of oxygen consumed by *Rh. meliloti* when grown in the media containing yeast extract in various concentrations are shown graphically in figure 2. Although smaller amounts of oxygen were consumed by this organism than by *Rh. trifolii* when grown in yeast extract media, the same general effects were exhibited. There was little or no growth

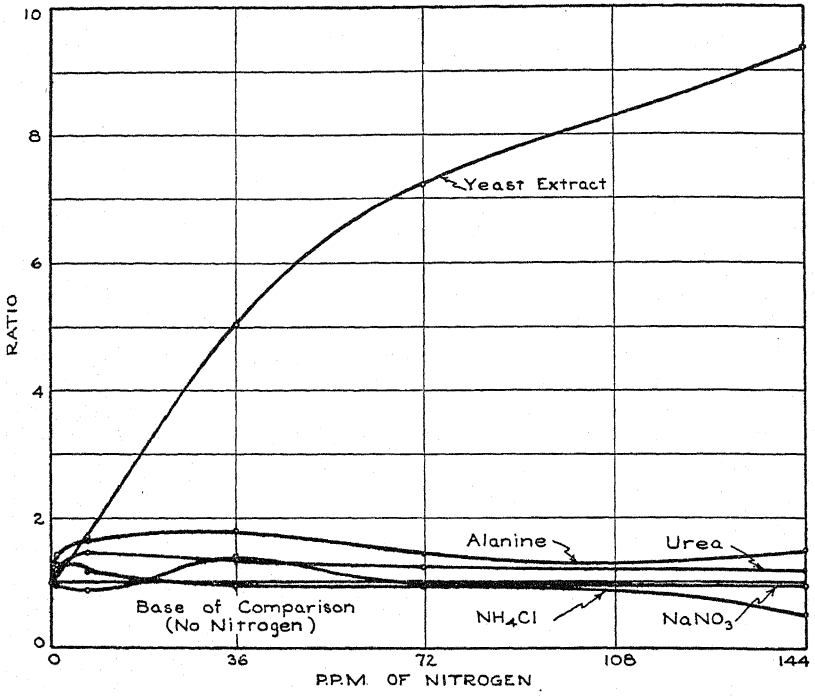


FIG. 1. THE RATIOS OF THE AMOUNTS OF OXYGEN CONSUMED BY *Rhizobium trifolii* IN THE VARIOUS NITROGENOUS MEDIA TO THAT CONSUMED IN THE MEDIUM WITHOUT NITROGEN

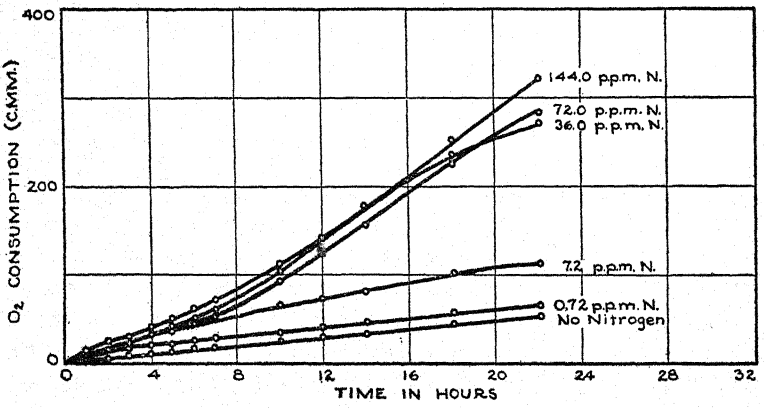


FIG. 2. OXYGEN CONSUMPTION BY *Rhizobium meliloti* IN MEDIA CONTAINING YEAST EXTRACT

in the medium without combined nitrogen, but the organisms continued to respire and consume oxygen at a fairly uniform rate throughout the entire period of study. On the other hand, the yeast extract definitely stimulated

growth, and increased the rate of respiration at least where the larger amounts were present, for a period of about 12 to 14 hours. The rate of increase, however, did not appear to be quite so great as in the case of *Rh. trifolii*. As was the case with the other species, after the organisms passed the logarithmic period of growth, the rate of oxygen consumption became fairly uniform or decreased slightly, indicating that the organisms were in the resting state, and probably that some were dead. It is also quite probable that no growth was taking place during this period.

When *Rh. meliloti* was grown in media containing the other forms of nitrogen, entirely different results were obtained from those in the experiments with *Rh. leguminosarum* and *Rh. trifolii*. The organisms of this species were definitely stimulated by ammonium chloride, sodium nitrate, urea, and ala-

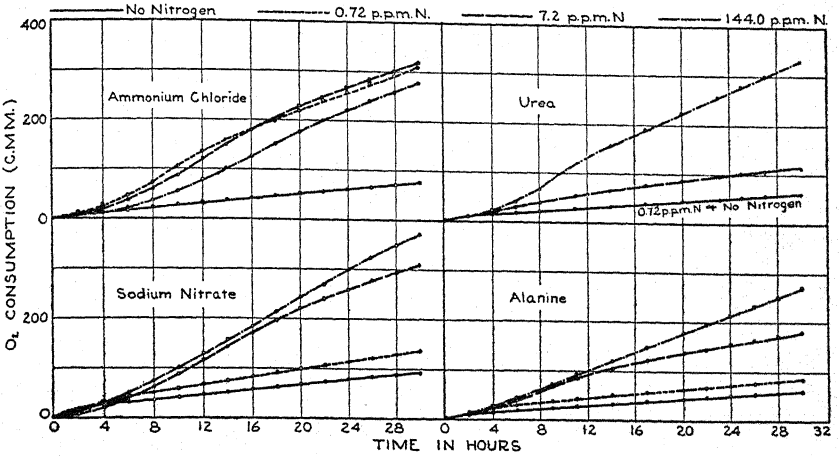


FIG. 3. OXYGEN CONSUMPTION BY *Rhizobium meliloti* IN MEDIA CONTAINING AMMONIUM CHLORIDE, SODIUM CHLORIDE, UREA, AND ALANINE

nine, and considerably larger amounts of oxygen were consumed during the period of the test. This is shown by the curves in figure 3.

There was a definite and rapid increase in the rate of oxygen consumption in the medium containing 0.72 p.p.m. of nitrogen as ammonium chloride. The maximum rate, about 17 c.mm. of oxygen per hour, was reached between the eighth and tenth hours, then there was a rather marked decline in rate to about 10 c.mm. per hour by the fifteenth hour. From that time on the rate was fairly uniform until the end of the experiment. The rate of increase was less in the medium with 144.0 p.p.m. of nitrogen as ammonium chloride, but continued for a little longer period before the maximum was reached between the fifteenth and eighteenth hour, when oxygen was being consumed at the rate of about 13 c.mm. per hour. From that time on there was a gradual decrease in the rate of consumption until the end of the test. The intermediate amounts of nitrogen employed produced intermediate effects.

Ammonium chloride in all concentrations stimulated oxygen consumption and growth. The smallest amount of ammonium chloride was just as effective as the larger amounts, and even more effective than the largest amount used, 144.0 p.p.m. of nitrogen, which it appears was a larger amount than the organisms could endure for maximum oxygen consumption.

Likewise, oxygen consumption by *Rh. meliloti* was very definitely stimulated by the addition of sodium nitrate to the basic medium. There was an increase in the rate of oxygen consumption during the first 10 or 12 hours, and presumably at that time the organisms were growing. The rate of increase was somewhat proportional to the amount of sodium nitrate in the medium. After the organisms passed the logarithmic period of growth, presumably they passed

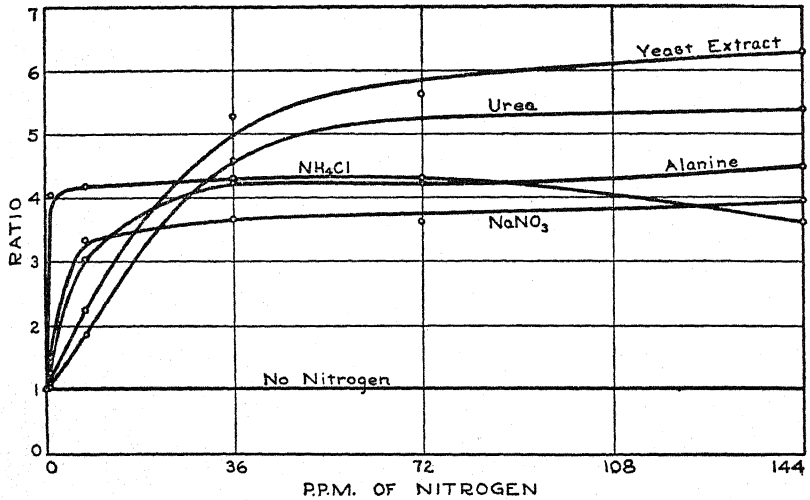


FIG. 4. THE RATIOS OF THE AMOUNTS OF OXYGEN CONSUMED BY *Rhizobium meliloti* IN THE VARIOUS NITROGENOUS MEDIA TO THAT CONSUMED IN THE MEDIUM WITHOUT NITROGEN

into a state of rest and continued to respire at a fairly constant rate for the remainder of the experiment. The total amount of oxygen consumed was considerably larger than when the other species of the genus were grown in the sodium nitrate media.

Similarly, urea and alanine definitely increased the rate of oxygen consumption by the organisms over that in the medium without nitrogen, the maximum rate being proportional to the amount of the nitrogenous materials in the media. This indicates that the nitrogen stimulated growth and that in its presence the organisms were presumably actively multiplying, whereas in the medium without nitrogen they were in a resting state throughout the entire period except, perhaps, for the first hour or two after inoculation, while the nitrogen carried over in the inoculum was being used.

The comparative effects of the different nitrogen sources on oxygen consumption by *Rh. meliloti* are shown in figure 4. The curves in this figure represent the ratio of the amount of oxygen consumed by the organisms in the different nitrogenous media at the end of 22 hours compared with that consumed in the medium without added nitrogen. About the same type of curve is shown for the yeast extract media as was shown for *Rh. trifolii* in figure 1. The curves for the other types of nitrogen are, however, very different. Those in figure 1 indicate that ammonium chloride, sodium nitrate, urea, and alanine had little, if any, stimulation on oxygen consumption and growth of *Rh. trifolii*, whereas the same forms of nitrogen very definitely stimulated oxygen consumption and growth of *Rh. meliloti*.

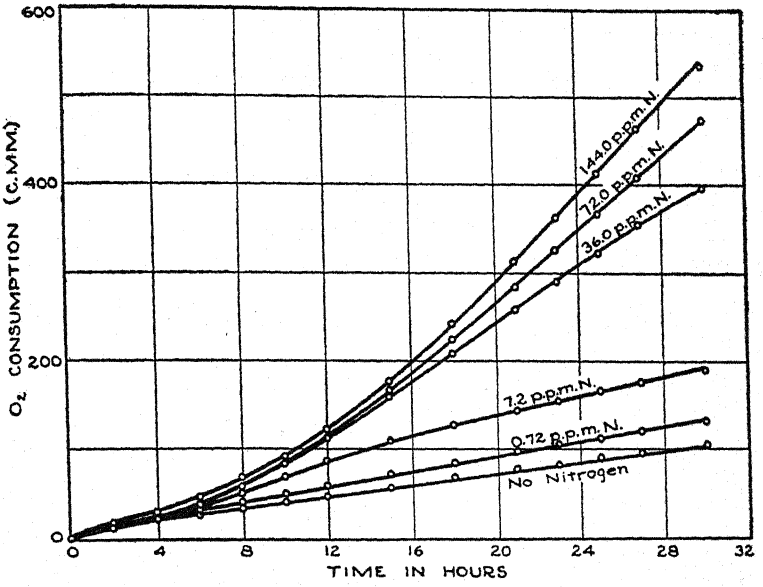


FIG. 5. OXYGEN CONSUMPTION BY *Rhizobium phaseoli* IN MEDIA CONTAINING YEAST EXTRACT

Rhizobium phaseoli.—The results of the oxygen consumption experiments with *Rh. phaseoli* in the various nitrogenous media are shown graphically in figures 5, 6, and 7.

In general, these results are similar to those obtained in the tests with *Rh. trifolii* and *Rh. leguminosarum*. Yeast extract definitely increased the rate of oxygen consumption by the organisms and presumably stimulated growth and multiplication to the same extent. The increase in rate of consumption was directly correlated with the concentration of yeast extract in the medium.

The other nitrogenous materials—ammonium chloride, sodium nitrate, urea, and alanine—had little or no effect on the rate of oxygen consumption. As may be observed, the curves for the nitrogenous materials in figure 6 in prac-

tically every case are very close to the no-nitrogen curve, thus indicating that the cells in the various nitrogenous media were in the same state, which was undoubtedly a resting state, as in the medium without nitrogen. Again, however, there is some evidence that ammonium chloride in the highest concentration used depressed slightly the consumption of oxygen by this organism as it did with *Rh. trifolii* and *Rh. leguminosarum*.

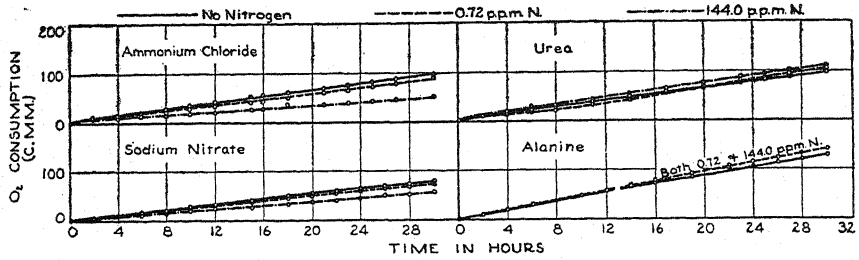


FIG. 6. OXYGEN CONSUMPTION BY *Rhizobium phaseoli* IN MEDIA CONTAINING AMMONIUM CHLORIDE, SODIUM NITRATE, UREA, AND ALANINE

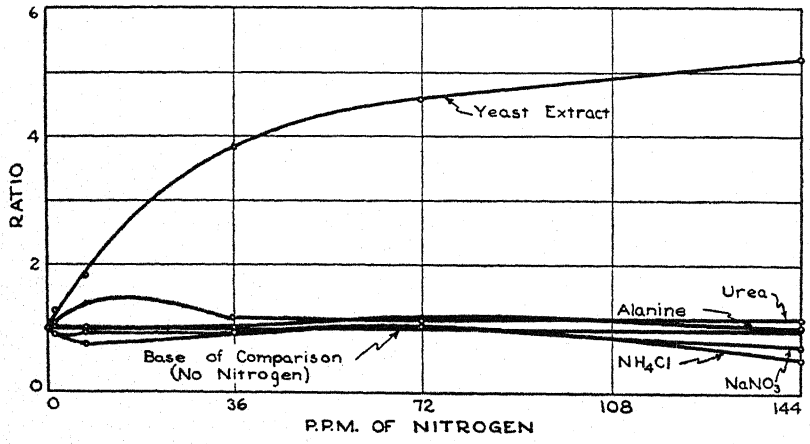


FIG. 7. THE RATIOS OF THE AMOUNTS OF OXYGEN CONSUMED BY *Rhizobium phaseoli* IN THE VARIOUS NITROGENOUS MEDIA TO THAT CONSUMED IN THE MEDIUM WITHOUT NITROGEN

SUMMARY AND CONCLUSIONS

Experiments similar to those with *Rh. leguminosarum* have been conducted with other species of the genus; namely, *Rh. trifolii*, *Rh. meliloti*, and *Rh. phaseoli*, to study the effects of various nitrogen sources on oxygen consumption. The results indicate that, in general, oxygen consumption and therefore growth of *Rh. trifolii* and *Rh. phaseoli* are affected in the same manner as in

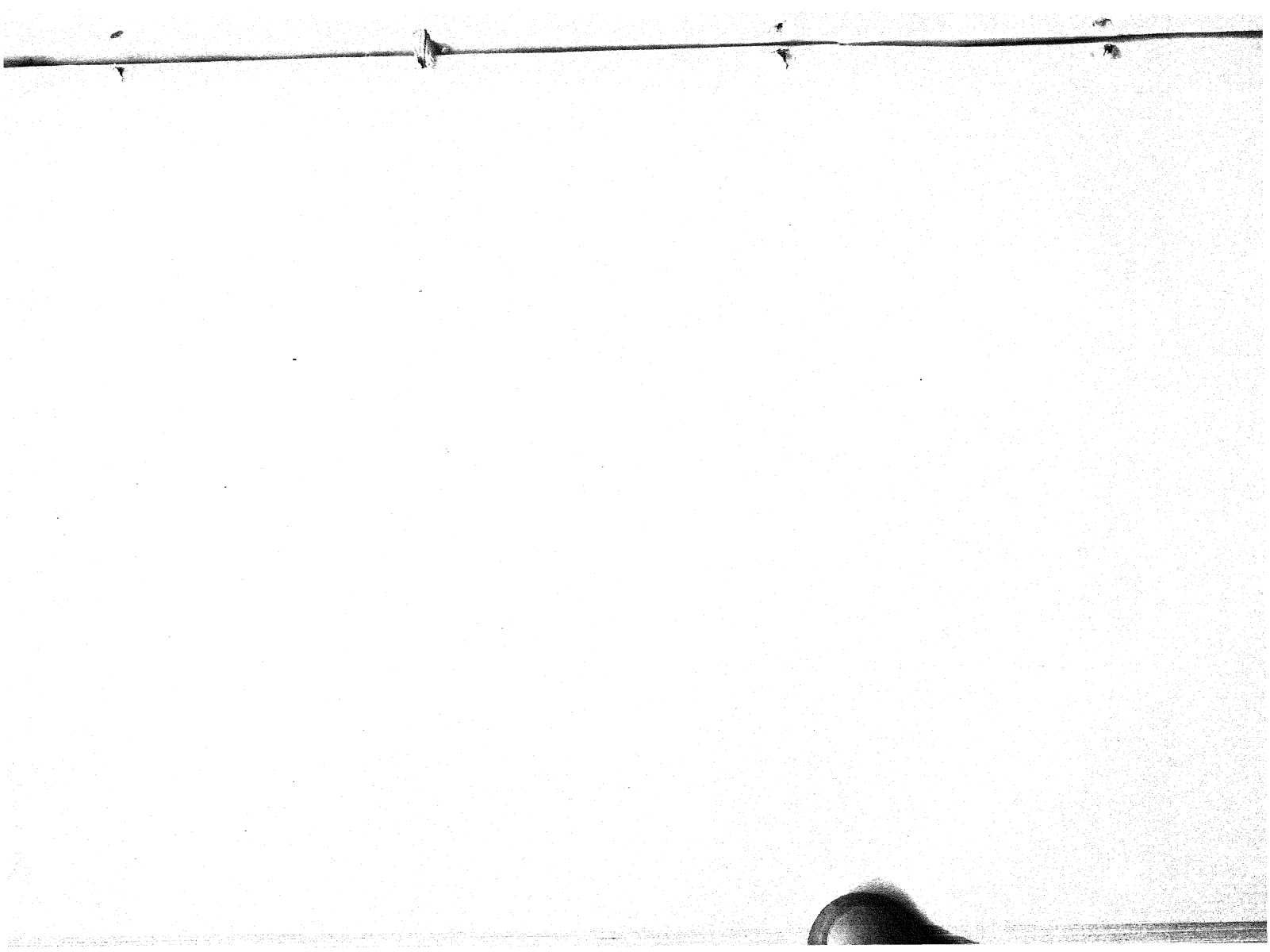
the case of *Rh. leguminosarum*. On the other hand, it seems that *Rh. meliloti* reacts entirely differently to the compounds of nitrogen, ammonium chloride, sodium nitrate, urea, and alanine, but in about the same manner to the yeast extract, which is a complex material containing only about 7.6 per cent nitrogen.

The reason for this physiological difference in the organisms of the different species has not yet been explained satisfactorily. Neither is it known whether, after a statistical analysis of physiological reactions of several species, the same general conclusions could be applied to the species as a whole, or whether certain reactions could be definitely linked with the efficiency of certain strains of the organisms in fixing nitrogen symbiotically. These points are being considered further, and it is hoped that additional information concerning the nitrogen nutrition and metabolism of this genus of microörganisms may be obtained.

REFERENCES

(1) WALKER, R. H., ANDERSON, D. A., AND BROWN, P. E. 1934 Physiological studies on Rhizobium: I. The effect of nitrogen source on oxygen consumption by *Rhizobium leguminosarum* Frank. *Soil Sci.* 37: 387–401.

(2) WARBURG, OTTO 1926 Über den Stoffwechsel der Tumoren. Julius Springer, Berlin.



ANION EXCHANGE: I. ADSORPTION OF THE PHOSPHORIC ACID IONS BY SOILS

S. RAVIKOVITCH

Jewish Agency Agricultural Experiment Station, Rehoboth, Palestine

Received for publication September 5, 1933

The adsorption of phosphate by soil has received considerable attention. The fixation by soil has been attributed to the insolubility of the compound formed with iron, aluminum, calcium, and magnesium. More recent investigations have transferred the problem from the field of purely chemical to the field of physico-chemical reactions. Mattson (3, 5) has shown the interrelationship of adsorption of phosphate with the electrokinetic behavior of soil colloids, and the properties of the mutual exchange between various anions (4).

Since cations are exchanged in the soils in nearly equivalent quantities, it would be of considerable interest to establish whether there exists such a law for anion exchange. To attempt to establish such a law, to compare anion exchange with cation exchange, and to study the rôle of the exchangeable cations in the process of anion adsorption are the purposes of this investigation.

SOILS

The experimental work was carried out with four different soils. The two Palestinian soils were obtained from the Kefar-Jehoshua of the Esdraelon Valley, and from the experimental plots of the Agricultural Experiment Station, Rehoboth. The Sharkey and the peat soils were obtained from the New Jersey Agriculture Experiment Station, U. S. A. The mechanical and chemical analyses of the Palestinian soils, together with the base exchange capacity are presented in tables 1 and 2.

All the soils differ widely in their chemical and mechanical composition as well as in their total exchange capacity. The exchange complex of the two Palestinian soils is almost entirely mineral since there is hardly any organic matter in the red sandy soil, and it is scanty in the Esdraelon soil. The exchange complex of the peat is rendered entirely organic, the mineral complex being destroyed by previous treatment with acid. All the soils were converted into H-soils, the Sharkey soil by electrodialysis (2) until all the exchangeable bases were removed, and the Palestinian soils by extraction with a 0.05 *N* solution of hydrochloric acid (1). The peat soil was treated continuously with a 2 per cent solution of boiling hydrochloric acid, and the mineral complex was thus destroyed. After the acid treatment, the soils were washed with distilled water until no free chlorine was present. Ca-soils were prepared from the H-soil by shaking periodically with a solution of $Ca(OH)_2$ for 1 or 2 days. The

soil with the solution was then transferred into dishes and evaporated to dryness. The soil was ground and passed through a 1-mm. sieve.

EXPERIMENTAL

The adsorption experiments were conducted on the air-dry soil, the volume of solution used being always corrected for hygroscopic moisture so that the total volume was 50 cc. The samples were shaken in small bottles for an hour in an automatic shaker with either phosphoric acid or ammonium phosphate, and subsequently allowed to stand for 4 days. This period of contact was

TABLE 1

Mechanical analysis of the soils

SOILS	FINE GRAVEL	COARSE SAND	MEDIUM SAND	FINE SAND	VERY FINE SAND	SILT	CLAY
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Clay soil of Esdraelon Valley (Kefar Jehoshua).....	Passed through a 1-mm. sieve	0.04	0.10	10.15	15.17	19.77	54.77
Red sandy soil of Rehoboth...	0.05	1.15	5.28	66.91	3.46	2.55	20.06

TABLE 2

Chemical analysis of soils and base exchange capacity

SOILS	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	ORGANIC MATTER	CO_2	BASE EXCHANCE CAPACITY M.E. IN 100 GM. SOIL
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
Clay soil of Esdraelon Valley (Kefar Jehoshua).....	64.98	15.17	8.85	2.17	2.91	0.18	0.86	Traces	51.60
Red sandy soil of Rehoboth.....	88.27	5.51	2.99	0.87	1.08	0.10	0.15	Traces	10.48
Sharkey.....									39.10
Peat.....									132.40

quite sufficient to achieve equilibrium between the soil and phosphoric acid. After 4 days of settling, the supernatant liquid was withdrawn and analyzed, the phosphoric acid being determined gravimetrically, the pH colorimetrically, and calcium as the sulfate in alcoholic solution. All the calculations were made on the basis of oven-dry weight.

Adsorption of phosphoric acid by H-soils

The experiments were carried out with both hydrogen and calcium soils of three different kinds: Esdraelon, Sharkey, and red sandy soil. The H-soils

were shaken with H_3PO_4 or with nearly neutral ammonium phosphate solutions; the Ca-saturated soils were treated only with ammonium phosphate solutions.

The results for the H-sandy soil (series 1) are presented in table 3. As would be expected, the adsorption increases with increasing phosphate concentration, but shows considerable discontinuity, the increase taking place at irregular intervals. Thus in the experiments 3, 4, and 5, where the concentrations of H_3PO_4 vary from 6.00 to 12.00 m.e., the amount of adsorbed PO_4 fluctuates only within the limits of 1.19 to 1.22 m.e. Again at concentrations of 15.00, 17.00, and 20.00 m.e. of phosphoric acid, the quantities adsorped are close to one another; namely, 1.90, 2.01, and 2.00 m.e. respectively. The intermediate

TABLE 3

Adsorption of phosphoric acid ions by a H-sandy soil from solutions of H_3PO_4 of various concentrations

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	PO_4 ADSORBED BY 7.5 GM. OF SOIL	ADSORPTION THEORETICALLY CALCULATED*	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSOBED AND THAT THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	
1	2.00	0.71	(I) $0.786 \times 1 = 0.786$	−0.08	<2.8
2	4.00	0.82		+0.03	<2.8
3	6.00	1.20		+0.02	<2.8
4	10.00	1.19	(II) $0.786 \times 1.5 = 1.179$	+0.01	<2.8
5	12.00	1.22		+0.04	<2.8
6	13.00	1.63	(III) $0.786 \times 2.0 = 1.572$	+0.06	<2.8
7	15.00	1.91		−0.06	<2.8
8	17.00	2.01	(IV) $0.786 \times 2.5 = 1.965$	+0.04	<2.8
9	20.00	2.00		+0.03	<2.8

* The base exchange capacity of the sandy soil sample is 0.786 me.

amount of adsorption of 1.63 m.e. stands between the aforementioned two groups of figures.

Table 4 presents the results of adsorption experiments with the same soil from nearly neutral ammonia-phosphate solutions.[1] In this series (series 2) the concentration of the phosphoric acid is increased to 0.80 *N*. The general feature of the relationship between adsorption and concentration of solution is similar to that in the experiments of series 1. As a result of relatively high

[1] As a matter of fact, in the experiments with H-soils, when brought in contact with ammonia-phosphate solutions of different pH values, a part or all of the H ions of the complex are replaced by the NH_4 ions. As a result, NH_4(H)-soils are obtained. For convenience, throughout this paper the H-soils were so named, even after their contact with the ammonia-phosphate solutions.

concentrations of ammonia-phosphate, the adsorption becomes negative. Within the limits of the positive adsorption, the amounts of adsorption for concentrations 8.00 and 10.00 m.e. of PO_4 equal 0.78 and 0.76 m.e.; those for concentrations 13.00 and 15.0 m.e. equal 1.52 and 1.58 m.e.; and those for concentrations of 17.00, 20.00, and 23.00 are 1.88, 1.95, and 1.98 m.e., respectively, for a soil sample of 7.5 gm. In the experiments of series 2 with nearly neutral solutions, as in those of series 1 with acid solutions, the same type of adsorption curve is obtained.

TABLE 4

Adsorption of phosphoric acid ions by a H-sandy soil from ammonia phosphate solutions of various concentrations

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	PO_4 ADSORBED BY 7.5 GM. OF SOIL	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	ADSORPTION THEORETICALLY CALCULATED*	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
1	2.00	0.57	1.00			5.6
2	4.00	0.63	2.00			6.0
3	6.00	0.69	3.00			6.5
4	8.00	0.78	4.00	(I) $0.786 \times 1.0 = 0.786$	−0.01	6.6
5	10.00	0.76	5.00		−0.03	6.6
6	12.00	1.19	6.00	(II) $0.786 \times 1.5 = 1.179$	+0.01	6.7
7	13.00	1.52	7.08	(III) $0.786 \times 2.0 = 1.572$	−0.05	7.2
8	15.00	1.58	7.50		+0.01	6.7
9	17.00	1.88	9.27	(IV) $0.786 \times 2.5 = 1.965$	−0.09	6.8
10	20.00	1.95	10.90		−0.02	
11	23.00	1.98	12.51		+0.01	
12	30.00	0.07	15.00			6.7
13	33.00	−0.30	16.50			6.7
14	36.00	−0.30	18.00			6.7
15	40.00	−0.29	20.00			6.7

*The base exchange capacity of the sandy soil samples is 0.786 m.e.

The phenomenon of more or less constant amounts of adsorption from H_3PO_4 solutions of different concentrations is still more distinctly shown in series 3 (table 5). The H-Esdraelon soil and H-Sharkey soil also give a range of almost constant amounts of adsorption, for a series of solutions of increasing concentrations. Thus, the figures of adsorption for the solutions from 0.16 *N* to 0.46 *N* for the H-Esdraelon soil are close to one another, as is the case also with the figures of adsorption for solutions from 0.12 *N* to 0.20 *N* for the H-Sharkey soil.

Having indicated this tendency of the numbers representing the amounts of adsorption of the PO_4 to fall into groups, we shall examine the given figures in each individual group and the intermediate figure between these groups. It should be mentioned that the total base exchange capacities for the soil samples

TABLE 5

Adsorption of phosphoric acid ions from phosphoric acid solutions of various concentrations by H-clay soils

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	PO_4 ADSORBED BY THE SOIL SAMPLE	ADSORPTION THEORETICALLY CALCULATED*	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
H-Esdraelon soil:	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
1	1.00	0.68			3.1
2	2.00	1.11			<2.8
3	3.00	1.44			<2.8
4	4.00	1.58	(I) $1.548 \times 1.0 = 1.548$	+0.03	<2.8
5	6.00	1.82			<2.8
6	8.00	2.39	(II) $1.548 \times 1.5 = 2.322$	+0.07	<2.8
7	10.00	2.32		±0.00	<2.8
8	13.00	2.36		+0.04	<2.8
9	15.00	2.31		−0.01	<2.8
10	17.00	2.26		−0.06	<2.8
11	20.00	2.30		−0.02	<2.8
12	23.00	2.33		+0.01	<2.8
13	26.00	2.58			<2.8
H-Sharkey soil:					
1	2.00	1.54			2.9
2	4.00	2.54			<2.8
3	6.00	2.95	(I) $2.933 \times 1.0 = 2.933$	+0.02	<2.8
4	8.00	2.91		−0.02	<2.8
5	10.00	2.94		+0.01	<2.8

* The base exchange capacity of the 3.0-gm. Esdraelon soil samples is 1.548 m.e., and of the 7.5 gm.-Sharkey soil samples, 2.933 m.e.

of the red sandy soil, of the Esdraelon soil, and of the Sharkey soil equal 0.786, 1.548, and 2.933 respectively.

In the acid series of experiments with the H-red sandy soils, the adsorption, expressed in milliequivalents, begins with amounts close to the base exchange

capacity of the soil sample. With an increase in concentration, the adsorption figures increase to about one and a half the total base exchange capacity. With a further increase in concentration, the amount of adsorption of PO_4 is about double the base exchange capacity, and with a still further increase of the concentration the amounts of adsorption equal about two and a half times the exchange capacity of the complex.

In the experiments of series 2, which are carried out with neutral solutions, the amount of adsorption for the identical initial concentrations is less than the exchange capacity of the soil sample. The increase in the concentration of the solution gives an adsorption equal to about the total base exchange capacity; with a further increase, the amount of adsorption is almost equal to one and a half times the total base exchange capacity, in experiment 6; it reaches double the exchange capacity in experiments 7 and 8, and two and a half times the exchange capacity in experiments 9, 10, and 11. The still further increase in the concentration gives a negative adsorption.

In the experiments with the H-Esdraelon soil and H-Sharkey soil the amounts of adsorption increase gradually until they almost equal the base exchange capacity of the soil sample. Then, for the H-Esdraelon soil at solutions of 0.16 *N* to 0.46 *N*, figures are obtained which are equal about to one and a half times the base exchange capacity. A further increase of the concentration leads to an adsorption equal to about double the base exchange capacity (table 7, experiments with Ca-soils). The amounts of adsorption for the H-Sharkey soil from 0.12 to 0.20 *N* solutions about equal the base exchange capacity of the soil sample.

Column 4 in tables 3, 4, and 5 presents the theoretically calculated figures of 1.0, 1.5, 2.0, and 2.5 times the base exchange capacity of the sample. Column 5 gives the difference in milliequivalents between the PO_4 actually adsorbed and that theoretically calculated. The difference between these amounts is insignificant and is within the limits of experimental error.

In order to explain such a regular adsorption, which increases by halves of the total base exchange capacity for each consecutive group, we must take into account the fact that phosphoric acid does not dissociate at once into an anion of a higher valence and into a corresponding amount of cations, but dissociates into H_2PO_4, HPO_4 and PO_4 ions. The phosphoric acid, therefore, may be adsorbed from a solution either as a monovalent, divalent, or trivalent ion, or as a combination of all three. The adsorption of the phosphoric acid ions of the different valences depends upon various factors like the pH, the concentration of the solution, and the nature of the soil material.

For the first group of constant quantities of adsorption the amount of adsorbed PO_4 equals about the base exchange capacity of the soil sample. This is possible when the exchange between the phosphoric acid ions and the hydroxyl ions of the soil complex, which are in an equilibrium with the exchangeable bases, proceeds in equivalent amounts. In this case the phosphoric acid is adsorbed as trivalent ions. For the second group the amount of adsorbed

PO_4 equals about one and a half times the base exchange capacity of the soil. This would be the case if all the anions of the soil complex were replaced by the divalent phosphoric acid ions. The quantities of adsorption for the third and fourth groups are twice and two and a half times the exchange capacity of the soil samples respectively. In these cases the adsorption consists probably of a combination of phosphoric acid ions of the varying valences.

The established rule of the equivalent relationship between the adsorption of PO_4 and the base exchange capacity of the soil complex indicates that the cations and the anions, which are in a state of electrostatic equilibrium, are present in equivalent quantities. The equivalent exchange reaction, which is characteristic of the cations (1, 2), exists also for the anions.

The difference in character of adsorption among the various groups indicates the existence of definite forms of PO_4 adsorption. For the H-soils the four distinct groups represent four definite forms of adsorption.

The weak concentrations of the solution give smaller quantities of adsorption than the exchange capacity of the soil sample. Here too, as in the case of the complete forms of adsorption, the process of adsorption proceeds on the same principles of an equivalent anion exchange. However, because of the weak concentration of the phosphoric acid solution, the exchange between the anions of the soil complex and the phosphoric acid ions of the solution is incomplete. As the concentration of the phosphoric acid ions increases the anion exchange becomes complete.

Adsorption of phosphoric acid by Ca-soils

Series 4 and 5 (tables 6 and 7) present the adsorption of PO_4 from neutral ammonia phosphate solutions by sandy and clay Ca-soils. The soils are similar to those used in series 1, 2, and 3 where they appeared as unsaturated. The course of adsorption of PO_4 by the Ca-soils is in general similar to that of the H-soils. For the given series of Ca-soils, the curves representing the characteristic phenomenon of the distribution of the amounts of adsorption into groups are more distinct than in the H-soils (fig. 1). The quantities of adsorption of these groups are in definite ratios with the exchange capacity of the soil complex. These ratios for the five various forms of adsorption equal about 1.5, 2.0, 2.5, 3.0, and 3.5 respectively. These figures are much higher than those obtained for the H-soils with many identical concentrations of neutral or even acid solutions of phosphate. The character of adsorption for the Ca-soils is somewhat different from that for the unsaturated soils and has become complicated by the presence of Ca in the complex. The rôle which the exchangeable calcium plays in the given experiments is obvious. Its introduction into the complex increased the adsorption of the PO_4.

In some cases the amount of PO_4 adsorbed by H-soils equals that adsorbed by Ca-soils from solutions of identical concentrations. This is due to the fact that the Ca-soil and H-soil give, at similar concentrations, different forms of adsorption which yield equal amounts of adsorbed PO_4 (*see* tables 3, 5, 6, and 7

and fig. 1). This phenomenon depends upon three factors which affect the adsorption: (*a*) the pH of the solution; (*b*) the valence of the adsorbed phosphoric acid ion; and. as will be explained later, (*c*) the combination of the replaced exchangeable calcium with the phosphoric acid.

TABLE 6

Adsorption of phosphoric acid ions by a Ca-sandy soil from ammonia-phosphate solutions of various concentrations*

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 cc.	PO_4 ADSORBED BY 7.5 GM. OF SOIL	RATIO OF EXCHANGE Ca TO ADSORBED PO_4	ADSORPTION THEORETICALLY CALCULATED†	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
1	1.50	0.42				7.05
2	2.00	0.52				7.05
3	3.00	0.95				7.05
4	4.00	1.06				7.05
5	5.00	1.20	0.66	(I) $0.786 \times 1.5 = 1.179$	+0.02	7.05
6	6.00	1.17	0.67		−0.01	7.05
7	7.00	1.24	0.63		+0.06	7.05
8	8.00	1.51		(II) $0.786 \times 2.0 = 1.572$	−0.06	7.05
9	9.00	1.54			−0.03	7.05
10	10.00	1.49			−0.08	7.05
11	11.00	1.57			±0.00	7.05
12	13.00	1.58			+0.01	7.05
13	15.00	1.90		(III) $0.786 \times 2.5 = 1.965$	−0.07	7.0
14	17.00	1.98			+0.01	7.0
15	20.00	2.32		(IV) $0.786 \times 3.0 = 2.358$	−0.04	
16	23.00	2.41			+0.05	
17	26.00	2.72		(V) $0.786 \times 3.5 = 2.751$	−0.03	
18	30.00	2.73			−0.02	7.05
19	33.00	0.39				
20	36.00	0.38				6.9
21	40.00	0.44				6.9

* Ratio of PO_4 to NH_4 equals 1.0:0.5 m.e.

† The exchange capacity of the soil samples is 0.786 m.e.

In order to establish the rôle of the exchangeable calcium in the adsorption of the PO_4, the experiments (series 6) presented in table 8 were undertaken. For these experiments a concentration of the solution was chosen which yields an adsorption belonging to the first group of constant quantities for Ca-soils. In this series, samples of Ca-sandy soil were shaken with various amounts of

$Ca(OH)_2$ solution of a definite concentration. The calcium hydroxide was quickly adsorbed by the Ca-soil samples. In the solution only traces of calcium were left, just as in experiment 1 where the Ca-soil was shaken with distilled water only (table 9). Complete adsorption of calcium took place only at a definite concentration of $Ca(OH)_2$. The highest concentration of the $Ca(OH)_2$ solution, from which the calcium was completely adsorbed by a Ca-

TABLE 7

Adsorption of phosphoric acid ions by a Ca-clay (Esdraelon) soil from ammonia phosphate solutions of various concentrations*

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	PO_4 ADSORBED BY 3.0 GM. OF SOIL	RATIO OF EXCHANGE Ca TO ADSORBED PO_4	ADSORPTION THEORETICALLY CALCULATED†	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
1	2.00	0.79				7.0
2	4.00	1.57				7.0
3	6.00	2.09				7.0
4	7.00	2.31	0.67	(I) 1.548 × 1.5 = 2.322	−0.01	7.0
5	8.00	2.31	0.67		−0.01	7.0
6	9.00	2.32	0.67		±0.00	7.05
7	10.00	2.37	0.65		+0.05	7.05
8	11.00	2.33	0.66		+0.01	
9	13.00	2.90				
10	15.00	3.01		(II) 1.548 × 2.0 = 3.096	−0.09	6.9
11	20.00	3.02			−0.08	6.9
12	23.00	3.76		(III) 1.548 × 2.5 = 3.870	−0.11	6.9
13	26.00	3.90			+0.03	6.9
14	30.00	3.91			+0.04	6.9
15	33.00	4.70		(IV) 1.548 × 3.0 = 4.644	+0.06	6.9
16	36.00	4.58			−0.06	6.9
17	40.00	4.64			±0.00	6.9

* Ratio of PO_4 to NH_4 in the solutions equals 1.0:0.5 m.e.

† The exchange capacity of the soil samples is 1.548 m.e.

soil sample of 7.5 gm. equals 0.323 m.e. of Ca in 40 cc. of solution. The total amount of adsorbed calcium by the soil complex for the last experiment was brought to 1.109 m.e., which corresponds to 141.1 per cent of the total base exchange capacity for the soil sample, established at pH 7.0. The adsorbed calcium within the limits of the exchange capacity of the soil complex, and that which is above its limits, proved to be identical in relation to its exchange

properties. As a result of contact with neutral salt solutions it totally passed into the solution.

The Ca-soils in which the exchangeable calcium, in milliequivalents, exceeds the total base exchange capacity of the soil, established at pH 7.0, are designated as "over-limed" Ca-soils.

After all the prepared soil samples had been shaken with ammonium phosphate solutions, the amount of adsorbed PO_4 was measured. As the amount of adsorbed calcium increased, the adsorption of PO_4 increased. The ratio of

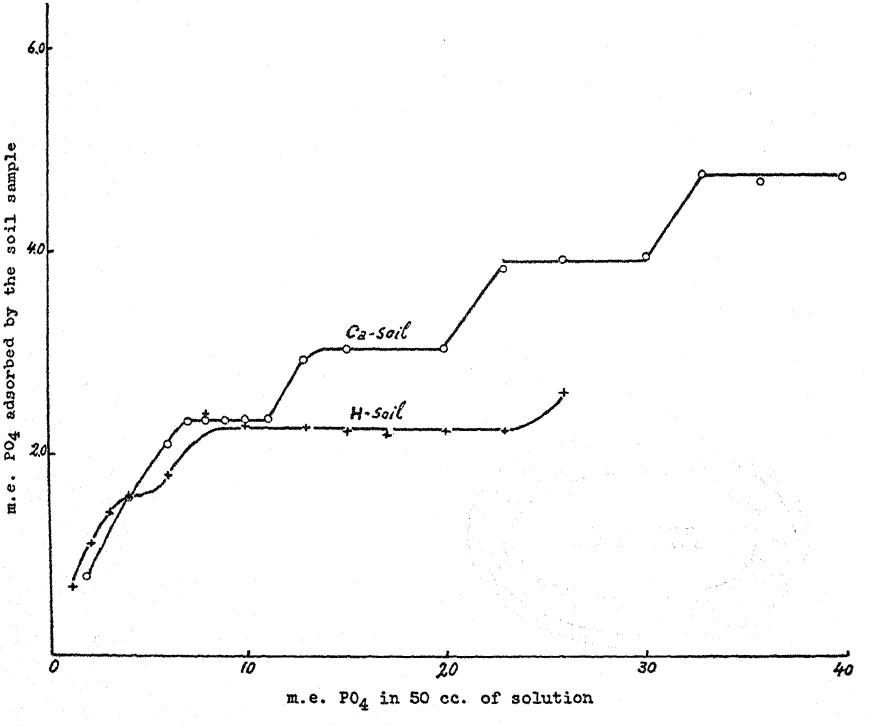


FIG. 1. ADSORPTION OF PHOSPHORIC ACID IONS BY A H-SOIL AND A CA-SOIL (FROM ESDRAELON VALLEY) FROM SOLUTIONS OF VARIOUS CONCENTRATIONS

the total amount of the exchangeable calcium to the amount of adsorbed PO_4 was found to remain the same as for the experiments with Ca-soils of the series 4 and 5 with concentrations yielding the first form of adsorption. This ratio is equal, or very close, to 0.67, which means that every 2 m.e. of adsorbed calcium tied 3 m.e. of phosphoric acid. The exact ratio in this case should be 0.666, but for practical purposes 0.67 is used. This constant ratio indicates the dependence of the adsorbed PO_4 upon the amount of exchangeable calcium.

Column 5, tables 6 and 7, and column 7, table 8, present the theoretically calculated amounts of PO_4 which should be adsorbed by a sample of either

Ca-soil or "over-limed" Ca-soil, when the adsorption depends only upon the amount of exchangeable calcium, i.e., when the PO_4 combines with the Ca in proportions of 3:2 m.e. The differences between the amounts of adsorption

TABLE 8

The adsorption of phosphoric acid ions by "over-limed" Ca-sandy soils

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE SOIL COMPLEX WITH CALCIUM		INITIAL CONCENTRATION OF PO_4 IN 50 CC.	PO_4 ADSORBED BY 7.5 GM. OF SOIL	RATIO OF EXCHANGE Ca TO ADSORBED PO_4	ADSORPTION THEORETICALLY CALCULATED ACCORDING TO THE RATIO OF $\frac{\text{m.e. exch. Ca}}{\text{m.e. ads. } PO_4} = 0.67$	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
	Per cent of base exchange capacity of the soil	M.e. of exchange Ca in the soil sample						
			m.e.	*m.e.*			*m.e.*	
1	100.0	0.786	6.00	1.17	0.67	1.18	−0.01	7.05
2	102.8	0.807	6.00	1.26	0.64	1.21	+0.05	7.05
3	106.7	0.839	6.00	1.30	0.65	1.26	+0.04	7.05
4	113.5	0.892	6.00	1.34	0.67	1.34	±0.00	
5	127.1	0.999	6.00	1.59	0.64	1.50	+0.09	
6	141.1	1.109	6.00	1.63	0.68	1.66	−0.03	

TABLE 9

Adsorption of Ca by a Ca-sandy soil from a $Ca(OH)_2$ solution

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF $Ca(OH)_2$ IN 40 CC. OF SOLUTION	FINAL CONCENTRATION OF Ca IN 40 CC. OF SOLUTION	pH
	m.e.	*m.e.*	
1		Trace	7.15
2	0.021	Trace	7.15
3	0.053	Trace	7.15
4	0.107	Trace	7.15
5	0.213	Trace	7.15
6	0.323	Trace	7.15

obtained by these experiments and the calculated amounts are insignificant. The regularity in the adsorption, which is expressed by the ratio

$$\frac{\text{exchange Ca}}{\text{adsorbed } PO_4} = 0.67$$

for the Ca-soils as well as for the "over-limed" Ca-soils, indicates that in both cases the nature of the combination of the exchangeable calcium with the adsorbed PO_4 is identical.

The character of the next forms of adsorption for the Ca-soils is altogether different (series 4 and 5). The ratio of adsorbed PO_4 to the base exchange capacity of the soil increases with each consecutive form of adsorption by about one half. The nature of adsorption for the consecutive forms and the

rôle of the exchangeable calcium in PO_4 fixation will be elucidated when the mechanism of the PO_4 adsorption for the different forms is discussed. The first and most important step in explaining this mechanism is to establish the fate of the exchangeable calcium when it comes in contact with the ammonium phosphate solutions. The question is whether there is a simultaneous combination of the exchangeable calcium with the exchange complex and the adsorbed phosphoric acid ions, or whether the Ca ions combine with the phosphoric acid only and thus break apart from the complex. Under neutral conditions, which is the case in the present experiments, it is impossible to solve analytically by a direct method the problem of calcium replacement in the presence of PO_4 in the solution. However, an indirect answer to the problem presented may be obtained from the results of the experiments presented in tables 10, 11, 12 and 13. These experiments were undertaken to investigate the in-

TABLE 10

Adsorption of phosphoric acid ions by a H-Sharkey soil from ammonium phosphate solutions of various pH values

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	PO_4 ADSORBED BY 7.5 GM. OF SOIL*	pH
	m.e.	*m.e.*	*m.e.*	
1	6.00		2.95	<2.8
2	6.00	2.00	2.88	3.3
3	6.00	3.00	2.76	3.9
4	6.00	4.00	2.47	5.5
5	6.00	5.00	2.46	5.8
6	6.00	6.00	2.20	>7.0
7	6.00	7.00	1.70	>7.0
8	6.00	7.88	1.33	>8.6

* The exchange capacity of the soil sample is 2.933 m.e.

fluence of the reaction and the degree of unsaturation of the complex on the PO_4 adsorption.

Influence of pH and degree of unsaturation of the complex on PO_4 adsorption

Table 10 (series 7) shows the adsorption of PO_4 by the H-Sharkey soil from ammonium phosphate solutions of various pH values. The pH was changed by introducing different amounts of ammonia into the solution. The variation of adsorption with changes in pH indicates the influence of the OH concentration on the adsorption of PO_4 by H-soils.

Series 8 (table 11) shows the adsorption by soils in which the exchangeable hydrogen is partially or completely replaced by calcium. The samples were shaken with slightly or strongly alkaline ammonium phosphate solutions. A difference in adsorption as influenced by the pH is noted, especially in the completely unsaturated samples and in those in which only 25 per cent and 50 per cent of the hydrogen ions were replaced by calcium. For the samples in which

75 per cent of the exchangeable hydrogen ions were replaced by Ca, only a very slight difference is noted in the adsorption of PO_4. No difference in the adsorption was obtained for the completely saturated samples. In the partly unsaturated soils, the ratio of exchangeable Ca to adsorbed PO_4 equals, or is close to, 0.67. The adsorption for these soils depends only on the amount of the exchangeable calcium, as was found in the case of the Ca-soils and "over-limed" Ca-soils.

As the amount of of the exchangeable calcium in the complex decreases, the ratio $\frac{\text{exchange Ca}}{\text{adsorbed } PO_4}$ becomes smaller than 0.67. If we assume that every 2 m.e. of exchangeable calcium combines with 3 m.e. of PO_4, as established for the Ca-soils at the same concentration of PO_4 in the solution (tables 6, 8), the

TABLE 11

Different degrees of saturation with Ca of the sandy soil and phosphoric acid ion adsorption from ammonium phosphate solutions of various pH values

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE SOIL COMPLEX WITH CALCIUM		RATIO OF PO_4 TO NH_4	PO_4 ADSORBED BY 7.5 GM. OF SOIL	RATIO OF EXCHANGEABLE Ca TO ADSORBED PO_4	pH
	Per cent of base exchange capacity of the soil	m.e. of Ca in the soil sample				
			m.e.	*m.e.*		
1	0.0	0.000	6.00:4.00	0.29		7.3
2	25.0	0.197	6.00:4.00	0.64	0.31	7.4
3	50.0	0.393	6.00:4.00	0.76	0.51	7.4
4	75.0	0.590	6.00:4.00	0.85	0.69	7.5
5	100.0	0.786	6.00:4.00	1.15	0.68	7.7
6	0.0	0.000	6.00:6.00	0.12		>8.6
7	25.0	0.197	6.00:6.00	0.53	0.37	>8.6
8	50.0	0.393	6.00:6.00	0.66	0.59	>8.6
9	75.0	0.590	6.00:6.00	0.88	0.67	>8.6
10	100.0	0.786	6.00:6.00	1.15	0.68	>8.6

amount of PO_4 combined with calcium can be calculated. By subtracting this calculated amount from the total amount of PO_4 adsorbed by the soil sample (table 11, experiments 2, 3, 7, 8), an excess of PO_4 will be obtained. This excess belongs to the PO_4 which is in combination with the part of the complex free from exchangeable calcium.

The adsorption of PO_4 by soils completely saturated with Ca is presented in series 9 (table 12). The pH of the solutions in this series of experiments fluctuates within wide limits. Changes in the pH within the limits of >8.6 to 6.4 did not influence the amount of adsorbed PO_4. The characteristic ratio of $\frac{\text{exchangeable Ca}}{\text{adsorbed } PO_4} = 0.67$, which was obtained for all pH values up to 6.1 inclusive, becomes smaller as the solution becomes more acid. At pH 6.1 re-

placed calcium appeared in the solution, and the amount increased with the decrease of pH. With the loss of a part of the exchangeable calcium the adsorption becomes more complicated. One part of the phosphoric acid combines with the Ca remaining in the complex, and the other one with the unsaturated part of the soil complex.

TABLE 12

Adsorption of phosphoric acid ions by a Ca-sandy soil from ammonium phosphate solutions of various pH values

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF THE PO_4 IN 50 CC.	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	PO_4 ADSORBED BY 7.5 GM. OF SOIL	RATIO OF EXCHANGE Ca TO ADSORBED PO_4	AMOUNT OF REPLACED Ca IN 50 CC. OF SOLUTION	AMOUNT OF EXCHANGE Ca LEFT IN THE SOIL COMPLEX	ADSORPTION THEORETICALY CALCULATED ACCORDING TO THE RATIO OF $\frac{\text{m.e. exch. Ca}}{\text{m.e. ads. } PO_4} = 0.67$	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*	*m.e.*		*m.e.*	*m.e.*		*m.e.*	
1	6.00	6.00	1.15	0.68		0.786	1.179	−0.03	>8.6
2	6.00	5.00	1.15	0.68		0.786	1.179	−0.03	>8.6
3	6.00	4.00	1.15	0.68		0.786	1.179	−0.03	7.7
4	6.00	3.00	1.17	0.67		0.786	1.179	−0.01	7.05
5	6.00	2.80	1.20	0.65		0.786	1.179	+0.02	6.7
6	6.00	2.60	1.15	0.68		0.786	1.179	−0.03	6.4
7	6.00	2.40	0.91	0.67	0.174	0.612	0.922	−0.01	6.1
8	6.00	2.20	0.75	0.62	0.325	0.461	0.691	+0.06	5.9
9	6.00	2.00	0.72	0.60	0.349	0.437	0.655	+0.06	5.4
10	6.00	1.80	0.72	0.54	0.395	0.391	0.587	+0.13	4.8
11	6.00	1.60	0.85	0.46	0.395	0.391	0.587	+0.26	4.1

TABLE 13

Adsorption of phosphoric acid ions, by a H-Sharkey soil partly saturated with calcium, from ammonia phosphate solutions of various pH values

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE SOIL COMPLEX WITH CALCIUM	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	PO_4 ADSORBED BY 7.5 GM. OF SOIL	pH
	per cent	*m.e.*	*m.e.*	*m.e.*	
1	75.0	6.00	5.00	2.91	7.4
2	75.0	6.00	6.00	2.61	7.6
3	75.00	6.00	7.00	2.48	>8.6
4	75.00	6.00	7.88	2.32	>8.6

The decrease of the absolute amount of adsorbed PO_4 as the pH decreases below 6.4 is explained by the gradual loss of the exchangeable Ca. While 2 m.e. of exchangeable calcium in Ca-soils fix 3 m.e. of PO_4, in H-soils, under similar conditions, 1 m.e. of the exchangeable anions of the complex is replaced by 1 m.e. of the PO_4 ions.

The ratio of $\frac{\text{exchangeable Ca}}{\text{adsorbed } PO_4} = 0.67$ is still retained for sandy soil samples having a Ca saturation in the limits of 75 per cent of their base exchange capacity. The limits of Ca saturation which produce such a ratio are entirely different for the Sharkey soil, the exchange capacity and composition of which differ from those of the red sandy soil. Electrodialyzed soil samples, after having been saturated with calcium to 75 per cent of their exchange capacity, were shaken with ammonium phosphate solutions of different pH values (table 13). The concentration of PO_4 in the solution is the same as in the previous series of experiments (tables 11, 12). At this concentration the PO_4 combines with the exchangeable calcium only in the ratio $\frac{Ca}{PO_4} = \frac{2}{3}$. However, at the same time an additional adsorption with the unsaturated part of the complex is observed. This can be judged from the changes in amount of adsorption with the changes in pH. Various forms of adsorption are thus obtained for the two different soils saturated to an equal degree by calcium. The lack of similarity in the forms of adsorption for these soils is directly related to the differences in the exchange capacity and the amount of the hydrogen ions present in the complex.

Mechanism of PO_4 adsorption by Ca-soils

From the experiments with Ca-soils, with "over-limed" Ca-soils, and with soils partially unsaturated with calcium (tables 6, 7, 8, 10, and 11), it is apparent that at the first form of adsorption the exchangeable calcium appears as the sole factor which regulates the amount of PO_4 adsorption. The adsorption regulated only by the exchangeable calcium is possible when the calcium does not split off from the soil complex when it comes into contact with the ammonium phosphate solutions. The union of the exchangeable calcium by its two valences with the phosphoric acid ions in the ratio of 2:3 would result in splitting off from the complex the newly formed salt which is practically insoluble, leaving behind a soil complex completely or partly unsaturated with calcium. The soil complex free from calcium would give, in turn, a new additional adsorption characteristic of H-soils. Such an additional adsorption however, is not observed. The connection between the exchangeable calcium and the complex is confirmed by the experiments on the influence of the pH on the adsorption by Ca-soils and H-soils.

The exchangeable calcium left in the complex combines simultaneously also with the adsorbed PO_4. Such a twofold connection is possible when one valence of the calcium ion remains in electrostatic equilibrium with one of its two hydroxyls, and the other valence with the phosphoric acid ion which had replaced its other hydroxyl. The phosphoric acid ion which replaces one of the two hydroxyls of the divalent calcium, giving with it the established ratio $\frac{\text{exchange Ca}}{\text{adsorbed } PO_4} = 0.67$, is the monovalent H_2PO_4 ion.

Table 14 explains the fate of the exchangeable calcium when it comes in contact with ammonium phosphate solutions yielding the second form of adsorption for Ca-soils. As the pH increases, the adsorption of PO_4 decreases. Such an adsorption is typical for H-soils and is possible for the Ca-soils only when the exchangeable calcium is split off from the complex; this occurs when it comes in contact with solutions of higher concentrations.

The process of complete replacement of the exchangeable calcium from the complex in the transitional stage between the first and second forms of adsorption, as seen in tables 6 and 7, occurs within narrow limits of concentrations for the red sandy soil, and within slightly wider limits for the Esdraelon soil.

TABLE 14

Forms of PO_4 adsorption at various H-ion concentrations

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	PO_4 ADSORBED BY THE SOIL SAMPLE	ADSORPTION THEORETICALLY CALCULATED*	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
Ca-sandy soil						
1	9.00	4.50	1.54	(II) $0.786 \times 2.0 = 1.572$	−0.03	7.08
2	9.00	6.00	0.94		−0.63	7.7
3	9.00	9.00	0.76		−0.81	>8.6
Ca-clay Esdr. soil						
1	15.00	7.50	3.01	(II) $1.548 \times 2.0 = 3.096$	−0.09	6.9
2	15.00	10.00	2.66		−0.44	
3	15.00	15.00	2.47		−0.63	>8.6

* The exchange capacity is 0.786 m.e. for the sandy soil samples, and 1.548 m.e. for the Esdraelon soil samples.

As the exchangeable calcium is being replaced from the complex under neutral conditions of the ammonium phosphate solutions, such as in the present experiments, it forms an insoluble tribasic salt of calcium phosphate. This salt contains PO_4 in quantities equal, in milliequivalents, to the exchange capacity of the soil complex. By subtracting from the total adsorbed PO_4 the amount which is bound to the replaced calcium, the amount of PO_4 adsorbed by the H-complex will be obtained. This amount for the second, third, fourth, and fifth forms of adsorption will equal about 1.0, 1.5, 2.0, and 2.5 times the exchange capacity of the soil complex, respectively. An identical order of adsorption, as influenced by the exchange capacity and the valence of the adsorbed anion, is established for the H-soils.

Negative adsorption of the phosphoric acid ion

The last regular form of adsorption for the red sandy soils occurs when the PO_4 combines with the complex in an amount which is equal to about 2.5 times the exchange capacity of the complex for the H-soils, and 3.5 times for the Ca-soils. As the concentration of the solution increases the adsorption becomes negative (tables 4 and 6). A definite positive amount of adsorbed PO_4 for the Ca-soil in the given case should be accounted for by its combination with the replaced calcium. The difference between the amount of PO_4 actually adsorbed and that which the replaced calcium should fix in its transition to tricalcium phosphate will give, for the Ca-soil samples, their negative adsorption values, which are close to those obtained for the H-soils at the same concentration of the solution. The phenomenon of negative adsorption depends not only on the definite concentration of the solution but also on the exchange capacity of the soil sample. That concentration of ammonium phosphate solution which gives a negative adsorption for 7.5-gm. samples of a sandy soil with an exchange capacity of 0.786 m.e. yields only the third form of adsorption for a 3-gm. sample of the Ca-clay soil with an exchange capacity of 1.548 m.e.

Speed of anion exchange reaction

Two series of experiments presented in table 15, were undertaken to determine the time necessary to establish an equilibrium between the phosphoric acid ions of an acid or neutral solution and the exchangeable hydroxyls of the exchange complex; in other words, to determine the speed of the anion exchange reaction. The experiments were made on Ca-soil and H-soil samples. The Ca-soils were brought in contact with a neutral ammonium phosphate solution, and the H-soils with a solution of H_3PO_4. According to their concentrations, the solutions yield the first form of adsorption for the Ca-soils as well as for the H-soils. In experiments 1 to 4 of both series, the soil samples were shaken with the solutions for 2, 5, 15, and 60 minutes, respectively. After this the solutions were immediately filtered to determine the amount of adsorbed PO_4. In experiments 5 to 7, the soil samples were shaken with the solutions for 1 hour but afterwards were left in contact with the solutions for 2, 4 and 6 days. After this time the upper clear solution was decanted and the amount of PO_4 determined. In spite of the fact that the solutions in both series of experiments are, according to their concentration of PO_4, very close to each other, the rapidity of anion exchange for the calcium saturated and unsaturated soils differs greatly. For the Ca-soils, the speed of exchange is very great. About 90 per cent of the hydroxyl ions which take part in the exchange are replaced by the H_2PO_4 ions in the first 2 minutes of contact between the soil and solution. However, a difference was observed for the H-soils where three hydroxyl ions of the complex are replaced by one trivalent PO_4 ion. In this case the replacement proceeded much more slowly, and a complete replacement of the exchangeable hydroxyl ions occurred only after 4 days of contact between the soil with the solution.

TABLE 15

The speed of anion exchange reaction

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	TIME OF CONTACT BETWEEN THE SOIL AND THE PO_4 SOLUTION	PO_4 ADSORBED BY THE SOIL SAMPLE	THEORETICALLY CALCULATED ADSORPTION ACCORDING TO THE FIRST FORM*	DIFFERENCE BETWEEN THE PO_4 ACTUALLY ADSORBED AND THAT THEORETICALLY CALCULATED	PO_4 ADSORBED IN RELATION TO PO_4 THEORETICALLY CALCULATED	pH
	m.e.	*m.e.*		*m.e.*	*m.e.*		*per cent*	
Ca-sandy soil								
1	6.00	3.00	2 min.	1.04		−0.14	88.2	
2	6.00	3.00	5 min.	1.07		−0.11	90.8	
3	6.00	3.00	15 min.	1.07	0.786 × 1.5 = 1.179	−0.11	90.8	
4	6.00	3.00	60 min.	1.12		−0.06	95.0	
5	6.00	3.00	48 hours	1.20		+0.02	101.8	
6	6.00	3.00	96 hours	1.17		−0.01	99.2	7.05
H-sandy soil								
1	4.00		2 min.	0.13		−0.66	16.5	<2.8
2	4.00		5 min.	0.25		−0.54	31.8	<2.8
3	4.00		15 min.	0.31		−0.48	39.4	<2.8
4	4.00		60 min.	0.31	0.786 × 1.0 = 0.786	−0.48	39.4	<2.8
5	4.00		48 hours	0.61		−0.18	77.6	<2.8
6	4.00		96 hours	0.80		+0.01	101.4	<2.8
7	4.00		144 hours	0.79		±0.00	100.0	<2.8

* The exchange capacity of the soil samples is 0.786 m.e.

TABLE 16

Adsorption of phosphoric acid ions, by a H-peat and a Ca-peat, from ammonium phosphate solutions of various pH values

EXPERIMENT NUMBER	INITIAL CONCENTRATION OF PO_4 IN 50 CC.	INITIAL CONCENTRATION OF AMMONIA IN 50 CC.	FINAL CONCENTRATION OF PO_4 IN 50 CC.	PO_4 ADSORBED BY 1.5 GM. OF PEAT*	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	
H-peat					
1	6.00		5.91	+0.09	<2.8
2	6.00	2.00	5.86	+0.14	
3	6.00	4.00	6.10	−0.10	<7.0
4	6.00	6.00	6.12	−0.12	>7.0
5	6.00	7.69	6.29	−0.29	>7.0
Ca-peat					
1	6.00		5.86	+0.14	3.0
2	6.00	2.00	5.89	+0.11	
3	6.00	4.00	6.09	−0.09	7.0
4	6.00	6.00	6.10	−0.10	>7.0
5	6.00	7.69	6.28	−0.28	>7.0

* The base exchange capacity of the peat samples is 1.986 m.e.

PO_4 adsorption by hydrogen and calcium organic exchange complexes

The organic exchange complex, in contrast to the mineral, possesses practically no capacity to adsorb PO_4 (table 16). A certain insignificant positive adsorption under acid conditions changes into a negative absorption as the neutral point approaches. In alkaline solutions the negative adsorption increases. The introduction of calcium into the organic exchange complex, a factor which increases the amount of PO_4 adsorption in the case of the mineral complex, did not change the adsorption in the present case. The degree of dissociation of the anions and cations of the exchange organic complex is probably very insignificant, and the connection of these ions with the organic complex is much more stable than with the mineral soil complex. This stability of connection of the exchangeable cations with the organic complex was observed in the experiments with acid solutions; the calcium remained entirely in the organic complex, whereas in the experiments with the mineral Ca-complex, at similar concentrations of PO_4 in the solution and at similar pH values, considerable amounts of exchangeable calcium passed into the solution as a result exchange with the H ions.

SUMMARY

The rôle of the mineral and organic exchangeable complexes and their exchangeable H and Ca cations in the adsorption of phosphoric acid ions is discussed. A detailed study is presented of the relationship between the amount of adsorbed PO_4 and its concentration in the solution, as well as of the dependence of this adsorption on the exchange capacity of the soil complex, on the amount of the exchangeable Ca and H, and on the pH of the solution.

The experiments were carried out on one peat and three mineral soils. Definite amounts of exchangeable calcium or hydrogen were introduced in their complexes, in accordance with the purpose of the experiment.

The mineral exchange complex. A general increase of PO_4 adsorption is observed with the increase of the concentration of PO_4 in the solution. In the case of comparatively low concentrations the amount of adsorbed PO_4 for H-soils and Ca-soils increases gradually. Beginning with a definite concentration, the quantities of adsorbed PO_4 distribute themselves into groups. Each group includes approximately equal amounts of adsorption.

In the H-soils there are four distinct groups representing four definite forms of adsorption. The amounts of adsorbed PO_4 for these four forms are equal in milliequivalents to about 1.0, 1.5, 2.0, and 2.5 times the exchange capacity of the soil sample respectively.

For the Ca-soils five forms of adsorption are established. The amounts of adsorbed PO_4 for them are equal in milliequivalents to about 1.5, 2.0, 2.5, 3.0, and 3.5 times the exchange capacity of the soil sample, respectively. These quantities are true only for soils the complex of which is completely saturated with calcium.

The existence of the different forms of adsorption is connected with the phenomenon of adsorption of phosphoric acid ions of different valences.

The adsorption of PO_4 by the soil complex proceeds on the principle of an equivalent anion exchange. The amount of adsorption depends on the anion exchange capacity of the soil complex (which is equal to the base exchange capacity) and on the valence of the phosphoric acid ions which take part in the adsorption.

In the first form of adsorption for the H-soils, there occurs an equivalent exchange between the exchangeable hydroxyls of the complex and the trivalent PO_4 ions. In the second form of adsorption, an equivalent exchange between the exchangeable hydroxyls of the complex and the divalent HPO_4 ions is proposed. For the third and fourth forms of adsorption there occur an equivalent exchange between the exchangeable hydroxyls of the complex and, probably, a combination of phosphoric acid ions of the various valences.

The first form of adsorption for Ca-soils is typical of comparatively low concentrations of ammonium phosphate solutions. In this form the amount of PO_4 adsorption is regulated only by the amount of the exchangeable calcium in the complex. Two milliequivalents of exchangeable Ca fix three milliequivalents PO_4, i.e., the ratio of $\frac{\text{m.e. exchange Ca}}{\text{m.e. adsorbed } PO_4} = 0.666\ (0.67)$. This ratio is established for Ca-soils as well as for the soils partially unsaturated with calcium and for soils the amount of exchangeable calcium of which exceeds the exchange capacity of the soil, established at pH 7.0. In the first form of adsorption, the exchangeable calcium is simultaneously connected with the exchange complex and the adsorbed phosphoric acid ion: its one valence is in an electrostatic equilibrium with one of its two hydroxyls, and the other valence with the monovalent H_2PO_4 ion.

In the other four forms of adsorption which follow the first one, the exchangeable calcium is replaced by the ammonium ions of the solution. The adsorption for these forms is twofold: (*a*) a combination of the PO_4 of the solution with the replaced exchangeable calcium in the form of an insoluble tricalcium phosphate salt, and (*b*) adsorption of the PO_4 by the $NH_4(H)$-complex, which is formed with the loss of the exchangeable calcium. The character of adsorption by this $NH_4(H)$-complex for the last four forms is similar to that which is established for the H-soils. The valences of the adsorbed phosphoric acid ions in the last four forms for Ca-soils; namely, 2, 3, 4, and 5, correspond to the valences of the adsorbed phosphoric acid ions in the forms 1, 2, 3, and 4 of the H-soils respectively.

With comparatively high concentrations of the ammonium phosphate solutions the adsorption for the H-soils and Ca-soils becomes negative.

In all the established forms of adsorption for H-soils the amount of adsorbed PO_4 changes as the pH value of the solution changes.

The changes in pH between slight acidity and high alkalinity exert no influence on the PO_4 adsorption by Ca-soils, by soils unsaturated with calcium to

a certain degree, nor by soils the amount of exchangeable calcium of which exceeds the exchange capacity of the soil, established at pH 7.0. This statement is true when the adsorption proceeds only according to the first form for Ca-soils.

In the soils partially saturated with calcium, where the adsorption proceeds partly according to the first form for H-soils, and partly according to the first form for Ca-soils, the amount of adsorbed PO_4 is influenced by the pH.

The anion exchange reaction, in the first form of adsorption for Ca-soils, proceeds very rapidly. During the first few minutes of contact between the soil and the solution, 90 per cent of the exchangeable hydroxyls which take part in the exchange reaction are replaced by the monovalent phosphoric acid ions. In the first form of adsorption for the H-soils, the exchange reaction with the trivalent phosphoric acid ions proceeds much more slowly.

The hydrogen and calcium organic exchange complexes possess practically no properties of PO_4 adsorption. With transition from acid to neutral and alkaline pH, the adsorption becomes negative.

REFERENCES

(1) GEDROIZ, K. K. 1923 The hydrochloric acid method for determining in the soil the cations in an adsorbed condition. *Soil Sci.* 16: 473–474.

(2) MATTSON, SANTE 1926 Electrodialysis of the colloidal soil material and the exchangeable bases. *Jour. Agr. Res.* 33: 553–567.

(3) MATTSON, SANTE 1928 Anionic and cationic adsorption by soil colloidal material of varying $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ ratio. *Proc. and Papers First Internatl. Cong. Soil Sci. Comn.* II: 199–211.

(4) MATTSON, SANTE 1931 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459–495.

(5) MATTSON, SANTE 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 343–365.



A NOTE ON THE DETERMINATION OF TITANIUM IN SOILS[1]

J. S. JOFFE AND L. T. KARDOS

New Jersey Agricultural Experiment Station

Received for publication September 26, 1933

In a study conducted on the movement and translocation of soil constituents in the profile, the problem of a speedy and accurate method of determining titanium came up. It is known that in the sodium carbonate fusion method for the determination of soil constituents, not all of the titanium goes into solution. Some remains in the residue of the SiO_2 after the HF treatment. According to Hillebrand (1), as much as one-third of the total quantity of titanium might remain in the SiO_2 residue. Results with 35 soil samples analyzed by the authors show that the TiO_2 in the SiO_2 residue varies from one-eighth to two-thirds of the total amount.

In the routine method of analysis as given by Hillebrand for minerals the R_2O_3 precipitate on the entire sample is added to the platinum crucible in which the SiO_2 has been determined, ignited, weighed, the contents fused with $KHSO_4$, and the TiO_2 determined colorimetrically by adding H_2O_2 to the acidified solution, equal to about 5 per cent H_2SO_4.

This procedure is not applicable in soil determinations because the R_2O_3 precipitate on a 5-gm. sample—the usual size sample taken in soil analyses—cannot be conveniently determined, and it would be too bulky to handle in the crucible which contains the TiO_2 residue from the SiO_2. In the routine soil analyses an aliquot is taken for the R_2O_3 determination, but the ignition of the precipitate cannot be made in the platinum crucible because the residue in it comprises the TiO_2 of the entire 5-gm. sample. The procedure was therefore modified as follows:

The residue from the SiO_2 is fused with $KHSO_4$, and the TiO_2 is determined. An aliquot of the HCl filtrate obtained in the process of stabilizing the SiO_2 is then taken, the R_2O_3 precipitated, ignited in a platinum crucible, weighed, fused with $KHSO_4$, the TiO_2 determined, the figure for the TiO_2 multiplied by the aliquot factor, the result added to the figure on the TiO_2 in the SiO_2 residue, and the sum represents the total TiO_2 in the 5-gm. sample of soil.

If the error involved in the determination of the R_2O_3, resulting from not subtracting the TiO_2 from it, is not to be reckoned with,[2] then the procedure

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

[2] The error is with the Al_2O_3 figures, since the Fe_2O_3 is determined directly on a separate aliquot.

may be simplified. The TiO_2 in the SiO_2 residue is fused with $KHSO_4$, made up to a definite volume, an aliquot corresponding to that of the R_2O_3 is taken, added to the acidified fusion mixture of the R_2O_3, and the TiO_2 determined. The figure obtained is multiplied by the aliquot factor, and the result represents the total TiO_2. In this manner only one TiO_2 determination is to be made. The error caused by the TiO_2 in the Al_2O_3 figures is, however, sometimes very serious and should not therefore be neglected. To cite a concrete example: Some of the podzols in the Lakewood soil series contain as much as 1.1 per cent of TiO_2, whereas the Al_2O_3 amounts to 2.6 per cent. It may readily be seen what the error would be if the TiO_2 were not subtracted.

If the TiO_2 is to be determined on a soil, without the necessity of getting information on the R_2O_3 constituents, the procedure resolves itself into the following: One-gram sample is taken, digested with H_2SO_4, treated with HF, the residue taken up with H_2SO_4, and the TiO_2 determined.

TABLE 1

Comparison of the H_2SO_4 and $K_2S_2O_7$ fusion methods for the determination of TiO_2

SOIL LABORATORY NUMBER	TiO_2 DETERMINED BY	
	H_2SO_4 method	$K_2S_2O_7$ fusion method
	per cent	*per cent*
1	1.236	1.087
2	0.544	0.544
3	0.399	0.394
4	0.309	0.359
5	0.689	0.679
6	0.742	0.749

Sometimes it is merely necessary to determine the TiO_2 on the HCl filtrate. In such a case it was found most convenient and simple to convert the strongly colored $FeCl_3$ solution into the practically colorless $Fe_2(SO_4)_3$, and to determine the TiO_2 on that rather than to precipitate the R_2O_3, wash, ignite, and fuse with $KHSO_4$. The method was tested out on a number of samples, as shown in table 1, and it was found to check very well with the $K_2S_2O_7$ fusion method.

Hillebrand (1) states that the error introduced by Fe_2O_3, in consequence of the yellowish color of its sulfate solution, is practically negligible, unless the Fe_2O_3 content is over 5 per cent. The soils investigated contained in every instance between 5 and 6 per cent Fe_2O_3, which would entail subtracting 0.01 per cent or less from the per cent of TiO_2. On the other hand, Merwin's (2) correction for the bleaching effect of alkali sulfates, which are invariably present when the fusion method of soil analyses is used, would give a counterbalancing correction of 0.015 per cent or less varying with a TiO_2 content of 0.5 to 1.8 per cent. If the TiO_2 exceeds 2 per cent no correction is required.

REFERENCES

(1) HILLEBRAND, W. F. 1919 The analysis of silicate and carbonate rocks. U. S. Geol. Survey Bul. 700.

(2) MERWIN, H. E. 1909 Coloration in peroxidized titanium solutions with special reference to the colorimetric methods of estimating Ti and F. *Amer. Jour. Sci.* 28: 119–125.

SOIL PROFILE STUDIES: VI. DISTRIBUTION OF TITANIUM IN SOILS WITH SPECIAL REFERENCE TO PODZOLS[1]

J. S. JOFFE AND A. J. PUGH

New Jersey Agricultural Experiment Station

Received for publication September 26, 1933

Studies made by the senior author (7) on the movement and distribution of the soil constituents in the profile of podzol and podzolic soils brought out the importance of the respective ions in fixing the attributes of the soil type and its degree of maturity and development. Quantitative determinations of ion distribution afford a valuable index for the interpretation of the potential fertility of the soil, methods and practices of fertilization, and, under certain conditions, even tillage operations, as in the case of accumulation of bases and other constituents in the B horizon whereby subsoiling might be advisable. Among other ions titanium has been investigated, and the results obtained are the subject of this paper.

Data on Ti in soils.—Titanium is one of the very widespread elements in the earth's crust and of course also in soils. Taking the lithosphere by itself Ti is the ninth element in the order of abundance.

Of the early reports on the Ti content of soils mention should be made of the work by Dunnington (4), who collected soil samples from many parts of the world. He analyzed 80 specimens, the Ti content of which varied from 5.42 per cent TiO_2 in a dark red clay from Virginia to 0.32 to 0.63 per cent in a number of Russian chernozems.

Vernadskii (20) discusses the sources and distribution of Ti in soils and mentions the work of Dunnington as a reproach to the Russian pedologists for neglecting the Ti ion in soil analyses.

Pellet and Freibourg (15) report a 2 per cent TiO_2 content in an Egyptian soil under sugar cane cultivation. And McGeorge (10) reports a 5 per cent TiO_2 content for some normal Hawaiian soils. In some soils the TiO_2 content is as high as 34 per cent. These Ti-soils are characterized by a small quantity of Al and large quantities of ferrous iron.

Robinson (16) presents Ti data on 26 soil samples—13 surface soils and their respective subsoils. The analyses cover primarily the soils of the eastern part of the United States—southern and northeastern states. His figures show that usually the Ti content increases in the subsoil.

Somewhat later Geilmann (5) examined 30 different German soils, in which

[1] Journal series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

TABLE 1

Titanium and other constituents of some soils in the United States and Canada

(From Marbut's "Transcontinental excursion" as reported by various analysts)

NUMBER	LOCATION OF SOIL	SOIL TYPE	DEPTH	TiO_2	SiO_2	Fe_2O_3	Al_2O_3
			inches	*per cent*	*per cent*	*per cent*	*per cent*
1	Cabin Creek, Md.	Sassafras silt loam	0–2.5	0.34	87.83	1.76	3.92
2	Cabin Creek, Md.	Sassafras silt loam	4–20	0.29	90.57	1.11	4.77
3	Cabin Creek, Md.	Sassafras silt loam	20–32	0.34	80.74	2.25	10.58
4	Cabin Creek, Md.	Sassafras silt loam	33–60	0.29	82.03	2.25	8.57
5	Washington, D. C.	Leonardtown silt loam	1–4	1.10	85.48	2.10	6.23
6	Washington, D. C.	Leonardtown silt loam	4–18	1.20	82.17	3.74	8.14
7	Washington, D. C.	Leonardtown silt loam	18–28	1.18	90.40	2.42	3.60
8	Washington, D. C.	Leonardtown silt loam	36+	1.04	72.33	5.75	13.87
9	Mt. Airy, Ga.	Cecil silt loam	0–4	0.91	83.19	2.58	6.91
10	Mt. Airy, Ga.	Cecil silt loam	6–30	1.05	57.58	9.51	21.53
11	Mt. Airy, Ga.	Cecil silt loam	40–65	0.68	74.59	4.18	14.66
12	Green Hill, N. C.	Cecil clay loam	1–6	1.47	58.33	6.38	20.06
13	Green Hill, N. C.	Cecil clay loam	6–40	1.43	49.95	9.31	26.54
14	Green Hill, N. C.	Cecil clay loam	40–84	2.11	44.68	11.36	27.68
15	Green Hill, N. C.	Cecil clay loam	84+	1.23	51.39	5.56	24.72
16	Ashwood, Tenn.	Hagerstown silt loam	0–12	1.69	78.14	3.61	7.24
17	Ashwood, Tenn.	Hagerstown silt loam	12–20	1.41	78.10	3.59	9.14
18	Ashwood, Tenn.	Hagerstown silt loam	20–30	1.41	74.91	4.39	12.13
19	Ashwood, Tenn.	Hagerstown silt loam	30–42	1.52	72.16	5.82	13.18
20	Purdy, Mo.	Lebanon silt loam	0–6.5	1.08	84.24	2.74	5.79
21	Purdy, Mo.	Lebanon silt loam	6.5–11.5	0.94	83.27	2.26	7.89
22	Purdy, Mo.	Lebanon silt loam	11.5–21	1.08	80.05	2.42	10.13
23	Purdy, Mo.	Lebanon silt loam	21–26	1.08	84.55	2.84	7.25
24	Fairmont, Nebr.	Grundy silt loam	0–6	0.61	71.47	3.30	10.87
25	Fairmont, Nebr.	Grundy silt loam	6–15	0.67	71.54	3.47	11.34
26	Fairmont, Nebr.	Grundy silt loam	15–36	0.62	65.43	5.69	15.26
27	Fairmont, Nebr.	Grundy silt loam	36–44	0.58	70.08	4.35	14.02
28	Fairmont, Nebr.	Grundy silt loam	44–60	0.59	68.45	4.35	14.02
29	Lincoln, Nebr.	Grundy silt loam	0–6	1.66	73.96	2.42	9.61
30	Lincoln, Nebr.	Grundy silt loam	6–13	1.44	73.81	2.50	10.54
31	Lincoln, Nebr.	Grundy silt loam	13–15	1.66	74.51	2.74	10.72
32	Lincoln, Nebr.	Grundy silt loam	15–32	1.80	60.86	3.63	22.85
33	Olmutz, Kansas	Type not stated	0–4	0.54	73.49	2.72	10.83
34	Olmutz, Kansas	Type not stated	4–22	0.60	72.83	3.08	12.00
35	Olmutz, Kansas	Type not stated	22–32	0.55	68.71	4.22	14.66
36	Olmutz, Kansas	Type not stated	30+	0.58	67.75	3.93	13.83
37	Colby, Kansas	Colby silt loam	1–1.5	0.53	72.91	3.31	11.52
38	Colby, Kansas	Colby silt loam	4–5	0.52	70.14	4.42	12.93
39	Colby, Kansas	Colby silt loam	5–9	0.49	60.69	2.64	11.99
40	Colby, Kansas	Colby silt loam	9–40	0.52	62.64	3.28	11.68
41	Nevada	Type not stated	0–1.5	0.50	64.37	3.84	13.89
42	Nevada	Type not stated	1.5–4	0.47	61.69	3.87	13.77
43	Nevada	Type not stated	5–15	0.51	57.78	3.67	12.85
44	Nevada	Type not stated	16+	0.27	38.40	2.09	7.57
45	Indian Head, Sask.	Type not stated	0–4	0.52	60.51	5.11	12.74

TABLE 1–*Concluded*

NUMBER	LOCATION OF SOIL	SOIL TYPE	DEPTH	TiO_2	SiO_2	Fe_2O_3	Al_2O_3
			inches	*per cent*	*per cent*	*per cent*	*per cent*
46	Indian Head, Sask.	Type not stated	4–20	0.52	66.21	5.25	12.85
47	Indian Head, Sask.	Type not stated	20–30	0.51	59.51	5.21	12.79
48	Indian Head, Sask.	Type not stated	30–66	0.68	52.40	6.63	16.92
49	Marion Co. Ohio	Miami clay loam	0–7	0.84	74.61	3.25	10.86
50	Marion Co. Ohio	Miami clay loam	7–14	0.91	65.18	6.08	15.93
51	Marion Co. Ohio	Miami clay loam	14–28	0.85	62.88	6.10	17.32
52	Marion Co. Ohio	Miami clay loam	28–36	0.66	56.53	4.90	13.78
53	Westport, Ind.	Miami silt loam	0–.75	1.00	71.96	2.71	7.16
54	Westport, Ind.	Miami silt loam	.75–10	0.79	78.55	2.77	9.32
55	Westport, Ind.	Miami silt loam	10–33	0.69	72.31	4.57	12.86
56	Westport, Ind.	Miami silt loam	34–42	0.65	66.26	5.06	11.52

he found from a trace to 1 per cent of TiO_2. He also reports analyses on the TiO_2 content of a number of plants, among which potato tops had shown the highest quantity of TiO_2: 0.0186 per cent of the total dry weight, or 0.269 per cent of the total ash. In tables 1 and 2 data are compiled on the Ti content of some soils in the United States and other parts of the world. Inasmuch as the available analyses permit, a cross-section of the Ti content in the important soil zones is presented in these tables. Unfortunately very few analyses were found on the distribution of Ti in the soil profile. At best some reports give data on the Ti content of the soil at various depths which are not satisfactory for the elucidation of the movement and translocation of the soil constituents in the profile.

Besides the Ti figures those on the SiO_2, Fe_2O_3, and Al_2O_3 content are presented. They might serve as a guide in establishing the reactions involved in the distribution of Ti in the soil.

An examination of the data reveals two characteristic features: 1. The Ti content within the various soil zones differs from as low as 0.27 per cent (in the Nevada subsoil and in the immature soil from Rio de Janeiro, Brazil) to as high as 4.04 per cent (in the Central African soils) and even as high as 20.02 per cent (in the Hawaiian Ti-soils, which normally contain as much as 5 per cent). Such variations must be attributed to the Ti content of the parent material. 2. The Ti content of soils, especially the lateritic and laterites, in the tropics is generally, with a few exceptions which might be explained on the basis of intrazonality of soils, higher than in the soils of the temperate climate. This is due to the active weathering in the tropics whereby the more immobile constituents, like Fe and Al, remain behind in the process of leaching. TiO_2 with its distinct amphoteric behavior (it forms metatitanates as anhydrides of a weak acid and as a cation it forms the tetravalent salts, all of which are easily hydrolyzed) reacts similarly to the R_2O_3 constituents as shown presently. In tables 1 and 2 we see that in the soils of Cuba (the Norfolk series is more closely

TABLE 2

Titanium and other constituents of soils in various parts of the world

NUMBER	LOCATION	TYPE OF SOIL OR MATERIAL	DEPTH	TiO_2	SiO_2	Fe_2O_3	Al_2O_3
				per cent	*per cent*	*per cent*	*per cent*
1†	Croatia	Terra rossa	Surface	0.37*	36.85	12.9	28.1
2	Montenegro and Rumania	Terra rossa	Surface	0.38	50.8	9.5	16.5
3	Cuba	Matanzas clay	0–3″	1.46	46.23	8.66	23.77
4	Cuba	Matanzas clay	11–69″	1.30	43.66	12.43	29.03
5	Cuba	Matanzas clay	87–98″	1.33	43.58	11.06	29.69
6	Cuba	Matanzas clay	98–156″	1.18	43.63	10.21	31.08
7	Cuba	Matanzas clay	156–168″	0.13	6.13	1.26	3.31
8	Cuba	Nipe clay	0–26″	0.80	3.28	63.04	18.46
9	Cuba	Nipe clay	26–40″	0.26	2.25	69.56	11.13
10	Cuba	Nipe clay	40–156″	0.80	1.83	71.12	12.36
11	Cuba	Nipe clay	156–192″	0.80	1.55	68.10	14.66
12	Cuba	Parent material	192+″	0.05	41.93	7.84	2.00
13	Cuba	Truffin clay	0–4″	1.74	36.21	15.13	27.16
14	Cuba	Truffin clay	7–15″	0.81	38.67	14.70	29.92
15	Cuba	Truffin clay	26–88″	0.81	39.23	14.92	31.10
16	Cuba	Norfolk fine sandy loam	0–17″	0.42	88.55	2.65	4.66
17	Cuba	Norfolk fine sandy loam	17–30″	0.56	75.58	8.54	9.67
18	Cuba	Norfolk fine sandy loam	30–38	0.57	75.10	7.57	11.34
19	Rio de Janeiro	Immature soil	A	0.27	70.88	1.47	15.89
20	Rio de Janeiro	Immature soil	B_1	0.28	67.90	2.59	18.44
21	Rio de Janeiro	Immature soil	B_2	0.45	63.54	2.46	22.14
22	Rio de Janeiro	Immature soil	C	0.13	70.23	1.37	17.22
23	Central Africa	Type not stated	Surface	2.89	61.86	5.76	19.90
24	Central Africa	Type not stated	30″	0.56	65.38	4.38	20.38
25	Central Africa	Type not stated	Surface	1.40	39.30	4.84	12.44
26	Central Africa	Type not stated	12″	3.98	37.90	14.82	28.08
27	Central Africa	Type not stated	36″	4.04	38.20	14.60	28.74
28	Central Africa	Type not stated	72″	3.61	38.94	14.98	28.63
29	Colombo	Laterite	1 meter	1.23	33.87	19.69	26.57
30	Colombo	Laterite	2 meters	0.83	46.91	7.10	25.77
31	Colombo	Laterite	3 meters	0.88	48.73	18.88	16.07
32	Colombo	Laterite	5 meters	0.91	51.24	1.04	28.84
33	Colombo	Laterite	7 meters	0.67	63.89	2.33	18.87
34	Colombo	Gneiss	10 meters	0.88	64.42	4.21	17.25
35	Switzerland	Soil		0.43	70.30	4.23	12.63
36	Switzerland	Parent material		0.81	66.12	5.82	14.52
37	Switzerland	Soil		0.54	66.54	4.47	13.38
38	Switzerland	Parent material		1.09	61.20	0.27	16.19
39	Sweden	"Barunerde"	3–13 cm.	0.53	65.42	2.51	10.17
40	Sweden	"Barunerde"	15–32 cm.	0.59	70.00	3.31	11.97
41	Sweden	"Barunerde"	100–115 cm.	0.55	72.90	3.18	12.25
42	Egypt	Sugar cane soil	Surface	2.0 after Pellet and Fribourg (15)			
43	Hawaii	Ti-soil	Surface	18.84	after McGeorge (10)		
44	Hawaii	Ti-soil	Subsoil	20.02			
45	Germany	Clay		0.885	after Blanck and Geilmann (3)		
46	Germany	Kaolin		0.284			

* In 3 of these only traces of TiO_2 were reported.

† Samples 1 and 2 were adopted from Blanck (2); samples 3–18 from Bennett and Allison (1); samples 19–22 from Harrassowitz (6); samples 23–28 from Marbut (11); 29–34 from Harrassowitz (6); 35–38 from Niggli (14); 39–41 from Stremme (19) after Lundblad.

related to the yellow earths or brown earths, which are subject to the acid hydrolysis[2] of the podzolic process of soil formation), in the Cecil series of the United States, in the soils of tropical Central Africa, Hawaii, Egypt, and others the Ti content is high. The lateritic nature of the aforementioned soils is easily discerned from the figures on the SiO_2 and R_2O_3 content. On the other hand the soils of the temperate region—nos. 24–56 in table 1, the soils of Nebraska, Kansas, Nevada, Saskatchewan (Canada), Ohio, and Indiana, and nos. 35–41 in table 2, the soils of Switzerland and Sweden—show a low TiO_2 content, as compared with the tropical soils. We need not lose sight of the fact that in the tropical soils mentioned, the parent material (nos. 7 and 12, table 2) is very low in TiO_2. The high TiO_2 content in nos. 29–32, table 1—soils from Nebraska—is undoubtedly due to the high content of this constituent in the parent material.

As we attempt to evaluate the distribution of the TiO_2 in the profile the data in table 2 are of little value, except for the Cuban soils which indicate an accumulation of TiO_2 in the surface horizon, as evidenced by the Matanzas and Truffin families, using the nomenclature of Bennett and Allison (1). The Nipe, however, seems to show no specific accumulation in the surface horizon (the low TiO_2 content at a depth of 26–40 inches between two layers of a high TiO_2 content is very strange and no explanation can be offered).

From table 1, which gives analyses on some soils in the United States, a somewhat better idea about the distribution of TiO_2 at various depths in the profile may be had. Of course, it would have been much clearer, and a better interpretation would have been possible if the depths were arranged in the order of the natural horizons. As it is, some depths might include portions of A and B and C. And it is common knowledge among pedologists that there is a quantitative and in some soils also a qualitative difference in the colloidal complex of the respective horizons. Clay, for example, accumulates in the B horizon of certain soils, and the TiO_2 content of clay is higher than of any other fraction in the soil. Steinkoenig (18) presents analyses on the various separates of a number of soils, and in most cases the TiO_2 content is highest in the fine silt and clay. Robinson and Holmes (17) report an increase of TiO_2 in finer fractions of the colloids.

It will be noted that the soils which could be designated as podzolic (the R_2O_3 and SiO_2 content indicate that), such as the Sassafras, Cecil, Leonardtown, and Miami, show tendencies to accumulate TiO_2 throughout the profile in the same manner as the lateritic soils do, mention of which has been made before. And what is more significant, the highest accumulation of TiO_2 is, as a rule, associated with a high Fe_2O_3 content. We do know of the existence of ilmenite ($FeTiO_3$), and it is not at all improbable that the new formations in the B horizon of soils undergoing the podzol process of soil formation contain such a compound. Of course there are the possibilities of forming the phos-

[2] For a detailed discussion on the acid hydrolysis in the podzol process of soil formation the reader is referred to a paper by Joffe (8).

phate of Ti—$Ti(HPO_4)_2$. The similarity in accumulation of TiO_2 in podzolic and lateritic soils may be interpreted as another link in the chain of evidence on the genetic relationship of these two types of soil formation.

Experimental:—To get a clear notion of the mode of distribution of any ion we must establish the mobility properties of the ion, i.e., we must ascertain the conditions under which the ion becomes soluble, either in true solution or as in the colloidal sol state. The method used in establishing the conditions which determine the mobility of Ti was that of Mattson (13), which, perhaps, could be designated as the method of isoelectric precipitation.

The hydroxide of Ti as an ampholyte is electropositive in acid and electronegative in alkaline solutions, as may be seen from table 3.[3]

TABLE 3

The isoelectric precipitation in the Ti-hydroxide system

A. 10 m.e. $TiCl_4$ in 1000 cc. H_2O

B. 50 m.e. NaOH in 1000 cc. H_2O

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	7.0	Opal.	xx	+3.03	3.6
20	7.8	Opal.	xxx	+3.03	4.0
20	8.0	Slow	xxxx	+3.03	4.1
20	8.2	Rapid	xxxx	+1.16	4.6
20	8.4	Instant	xxxx	+0.61	4.6
20	8.5	Instant	xxxx	−1.21	5.0
20	8.6	Rapid	xxxx	−2.75	6.4
20	8.8	Slow	xxx	−3.03	6.7
20	9.0	Opal.	xxx	−3.03	7.4

Isoelectric pH 4.8.

It will be noted that in the presence of Cl the Ti is positive up to pH 4.6, and is isoelectric at pH 4.8. As pointed out by Mattson (13) the ampholytes as hydroxides are probably not pure hydroxides, but they contain the anion present in solution, the nature of which influences the isoelectric pH. Beginning with pH 3.6 some hydroxide forms, as shown by the flocculation data. With an increase in pH more and more of the hydroxide is formed, i.e., less Ti is in solution. With a change in charge—as the basicity of the medium increases—the Ti electronegative complex slowly increases its electrokinetic capacity and dissociates more and more as anionic complex. It is probable that it has a composition somewhat on the order of a titanate, perhaps as

[3] The headings of tables 3 and 4 illustrate the procedure. For a more detailed outline of the method the reader is referred to the papers by Mattson (13). Suffice it to say here that the charge and migration velocity of the colloidal complex were determined in the cataphoresis cell as worked out by Mattson (12).

NaTi(OH). It is thus clear that with the increase in pH beyond the isoelectric point in either direction—strongly positive at very low pH and strongly negative at high pH readings—Ti will be in solution and therefore mobile.

If we should bar any other side reactions and assume that the Ti moves in the soil profile as if it were in the hydroxide system, then it will be mobile either as a cation at very low pH values tending to become finally ionically dispersed, or as an anionic complex at high pH values. In the podzol process of soil formation where acid hydrolysis predominates the existence of titanates as in the hydroxide system is out of the question. The pH in the podzols or podzolic soils, as a rule, is far below 6.7, the point at which the anionic complex becomes soluble. As will be pointed out presently, the Ti might become mobile even at a pH below 6.7 in the presence of other anions, but for the moment we are considering the hydroxide system under which no soluble titanates are probably below pH 6.7. On the other hand we might very well expect that in the podzolic process of soil formation there would be locally in the soil acid spots, under the influence of nitrification or sulfur oxidation, where the pH is low enough to bring the Ti in solution as an electropositive ion.

In the lateritic process of soil formation where alkaline hydrolysis prevails the Ti might become mobile as an anionic complex. But apparently the reactions which prevent the mobility of the R_2O_3 constituents in the laterite profile are also instrumental in keeping back the Ti. This might explain why in most of the laterites, for which reliable analytical data are available, the Ti seems to accumulate in the surface horizon. It is probable that if any Ti appears in solution it forms in the laterite the insoluble titanates of iron, specifically the $FeTiO_3$ (ilmenite).

As has been pointed out, the possibility of Ti moving as a positive ion in the hydroxide system is within the range of reactions in the podzol profile. We must, however, remember that in the soil we have other anions, such as SiO_3, SO_4 and PO_4, which influence the mobility of such ampholytes as the R_2O_3 and TiO_2. The effect of anions on the precipitation of Fe and Al has been noted by Joffe and McLean (9), who have shown that in the presence of SO_4 the precipitation takes place at a lower pH than in the presence of Cl or NO_3 and with PO_4 the pH is still lower. It was Mattson (13), however, who explained the mechanism of this behavior.

If we examine the data in table 4 on the isoelectric precipitation of Ti in the phosphate system we note that the isoelectric pH has been displaced, in comparison with the hydroxide system, far over on the acid side. It is as low as pH 2.7–2.8. With an increase in pH the Ti complex as a negative ion is stable up to pH 6.0 and above that it again goes into solution. It is of interest to note that at pH 2.37 and 2.92 the precipitate which formed from 40 mgm. of TiO_2 in 200 cc. of H_2O and 24.2 mgm. of P_2O_5 consisted of all the Ti and only 5.16 mgm. of P_2O_5, or the molar ratio of $\frac{TiO_2}{P_2O_5}$ at these pH values is 13.7. With an increase in pH this ratio increases; at pH 3.8 the precipitate consists of all

the Ti and 4.0 mgm. of P_2O_5. At pH 6.8 both the Ti and PO_4 ions almost remain in solution as shown by the flocculation data.

From the researches by Mattson (13) on the isoelectric precipitation of the R_2O_3 it is clear that in the silicate system the isoelectric pH is slightly higher than in the PO_4 system, i.e., the PO_4 has a higher displacing power than the SiO_3, the latter having a lower dissociation constant than PO_4. One would therefore expect that in a soil containing free PO_4 and SiO_3 ions, provided both are quantitatively in the same order, the Ti would combine with the PO_4 rather than with the SiO_3. In the laterites the PO_4 and, especially, the SiO_3 ions are in circulation, but the pH environment is hardly favorable for the Ti to combine with them, since the isoelectric pH of both of these anions in combination with Ti is far below the one prevailing in laterites. It is, however,

TABLE 4

The isoelectric precipitation in the Ti-phosphate system

A. 20 cc. $TiCl_4$ (10 m.e. TiO_2 per liter)

B. 20 cc. Na_2HPO_4 (2.42 mgm. P_2O_5)

Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
m.e.	*m.e.*				
0.000	0.197	Rapid	xxxx		2.40
0.000	0.00	Rapid	xxxx	+slow	2.80
0.074	0.00	Rapid	xxxx	−1.51	3.09
0.098	0.00	Rapid	xxxx	−1.51	3.35
0.123	0.00	Rapid	xxxx	−2.02	3.71
0.137	0.00	Rapid	xxxx	−3.03	4.82
0.148	0.00	Turbid	Turbid		6.28

Isoelectric pH 2.9.

possible that in the presence of Ca it might form titanite, or sphene ($CaTiSiO_5$). It is probable that some of the little SiO_2 preserved in laterites exists as sphene. In the podzols, as shown in table 5, there seems to be nothing in the P_2O_5 figures to indicate any association with the Ti ion. It is probable, however, that in the presence of free SiO_3, as is the case in the A_2 and B_1 horizon, the Ti anionic complex should replace SiO_3, acting in this case as an anion. Mineralogists long ago suspected the substitution of TiO_2 for SiO_2, although they have never been able to point out the mechanism of the reactions involved. This would also explain the tendency of Ti to accumulate usually in the A_2 or B_1 horizon in the podzols and podzolic soils.

Another point to consider in the problem of the mobility of Ti in soils is the probable effect of the humate ions in the system. It is known that all soluble Ti-salts are hydrolyzed by H_2O, but in the presence of organic compounds the reaction is impeded. This means that the humates serve as protective agents

in keeping the Ti compounds in solution. The nature and conditions of the reactions between Ti and humates have not been studied, but they may be inferred from the behavior of the humates with the R_2O_3 constituents.

The humate ion complex is negatively charged and in combination with R_2O_3 is isoelectric at low pH values. The greater the concentration of humate to a fixed quantity of R_2O_3 the lower is the isoelectric pH. With a decrease of humate and an increase of R_2O_3 the isoelectric pH increases, as shown by Mattson (13). Similar reactions probably take place in the Ti-humate systems, and the isoelectric pH of the Ti-humus complex will be lower than in the corresponding Fe and Al complexes. In podzols where the quantity of soluble humus is at times high, as indicated by the movement in the profile and its accumulation in the B horizon, the Ti-humate complex would become soluble only at very high pH values or at very low pH values, since humates have a tendency to form two isoelectric points. With the total quantity of Ti generally being low, the possible reactions between Ti and humate will usually be similar to that of a high humate content in the complex. Under such conditions, for instance, 1 millimol of $AlCl_3$ and 3 millimols of Na-humate show that at pH 4.5 flocculation is instantaneous and only above that does it remain in solution; it begins to go into solution again at very low pH values. With 4 millimols of $AlCl_3$ and 3 millimols of Na-humate the isoelectric pH is between pH 4.8 and 5.8 and above that it is in solution. Which condition prevails in the soil is, of course, problematic. Some deductions might be made, but this is beyond the scope of this paper. It only brings out that under conditions of podzolization where the pH is usually low there are possibilities for the Ti to be translocated by the aid of the humus. We must also keep in mind the effect of other soluble ions like Ca and Mg which are absorbed in the base exchange complex and thereby shift the isoelectric pH.

If we turn our attention to table 5, where data are presented on a number of podzolic and two mature podzol soils, the picture of the distribution of Ti in the profile in the light of the data and discussion on isoelectric precipitation attains a new meaning and becomes more clear.

In the Lakewood podzols the slight increase in the B horizon might be attributed to the increase of the clay fraction by mechanical movement. And, as has been pointed out, the Ti content in the clay fraction is high. On the other hand the Ti increase in A_2 must be attributed to the translocation of Ti in one way or another, in the manner previously discussed in connection with isoelectric precipitation. In the process of hydrolysis the TiO_2 probably separates as rutile, which has been frequently reported in soils. There seems to be no definite correlation between the Fe and Ti distribution in the podzol profile as there is in the laterite profile. In the podzol we have a distinctly acid condition, as indicated by the low pH values. It is possible that in the complexity of reactions associated with the stability of the isoelectric precipitation the pH value prevailing in the podzol is favorable for the slight movement of Ti compounds, as outlined in the foregoing. The high humus

content in A_1 and the soluble humus compounds in A_2 would protect the TiO_2 and only at B_1 and B_2 would the compounds hydrolyze and deposit the TiO_2.

In the podzolic soils (the Dutches, Collington, and Sassafras), we note a definite accumulation of Ti in the B horizon. As in the Lakewood podzol this increase might be partially attributed to the higher clay content. If we compare the Ti content of the parent material (C horizon) and that of the upper horizons we note a distinct accumulation in the profile. In this respect the podzolic soils approach the condition existing in the laterite.

For the problem of classifying the podzolic soils in the United States, especially those which resemble the "Braunerde" and those close to the zone of the yellow earths, which in turn might be looked upon as a transition to the

TABLE 5

Partial analyses of some soils in the podzol zone

HORIZON	DUCHES LOAM				COLLINGTON LOAM				SASSAFRAS FINE SANDY LOAM			
	pH	TiO_2	Fe_2O_3	P_2O_5	pH	TiO_2	Fe_2O_3	P_2O_5	pH	TiO_2	Fe_2O_3	P_2O_5
		per cent	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*
A0	5.8	0.581	5.01	0.167	4.9	0.470	3.19	0.208	4.6	1.584	1.48	0.086
A1	6.8	0.679	4.78	0.204	4.7	0.556	3.67	0.168	4.8	1.787	2.37	0.031
A2	5.4	0.758	4.98	0.103	5.0	0.495	4.24	0.110	4.6	1.790	2.43	0.016
B1	5.8	0.749	6.62	0.140	4.9	0.625	5.98	0.154	4.7	1.592	2.73	0.024
B2	6.1	0.771	7.18	0.119	4.9	0.445	6.58	0.150	5.2			
C1	6.4	0.538	6.57	0.158	4.9	0.394	7.37	0.153	5.2	1.466	2.78	0.003
C2	...				4.9	0.359	6.78	0.073	...			
					LAKEWOOD SAND (FULLY DEVELOPED PODZOL)				LAKEWOOD SAND (DWARFED PODZOL)			
A1	...				4.8	1.064	1.3		4.2	0.544	0.72	
A2	...				4.8	1.039	1.1		4.6	0.594	0.69	
B1	...				5.1	1.088	1.9		4.9		1.23	
B2	...				5.2	1.190	1.9		5.0	0.544	1.66	
C	...				5.2	0.915	1.35		5.2	0.544	1.01	

lateritic process of soil formation, the Ti distribution in the soil profile may serve as another link in the relationships existing between the various soil zones.

In the distribution of any soil constituent in the profile the rôle of the colloids is of prime importance. Colloid analyses complete the picture obtained from data on total analyses of the soil as a whole. Unfortunately very few systematic studies have been made on the colloids of the various soil zones by the profile method. But from the data available on the colloids of soils and subsoils in the various parts of the United States some deductions might be made. For this purpose table 6 has been compiled from analyses made in the Bureau of Soils by Robinson and Holmes (17).

It will be noted that in the colloids of the soils from Georgia, North Carolina,

Mississippi, and Kentucky the TiO_2 content in the surface soils is invariably higher than in the subsoils. The reverse is true for the soils from Maryland, New York, Indiana, Iowa, and Nebraska: the TiO_2 content is lower in the colloids of the surface soil than in the subsoil. A general deduction suggests

TABLE 6

TiO_2 in colloid fraction of various soils in the United States

SOIL TYPE AND LOCATION	DEPTH	TiO_2
	inches	*per cent*
Cecil clay loam, Ga.	0– 9	0.62
	9–18	0.52
Norfolk fine sandy loam, N. C.	0– 8	0.79
	12–36	0.71
Orangeburg fine sandy loam, Miss.	0–10	0.54
	10–36	0.44
Clarksville silt loam, Ky.	0–10	0.81
	10–36	0.63
Sassafras silt loam, Md.	0– 8	0.63
	8–22	0.70
Huntington loam, Md.	0– 8	0.40
	8–30	0.47
Chester loam, Md.	0– 8	0.58
	8–32	0.70
Ontario loam, N. Y.	0–12	0.38
	12–22	0.56
Carrington loam, Ia.	0–12	0.47
	15–36	0.65
Marshall silt loam, Nebr.	0–14	0.48
	14–36	0.50
Miami silty clay loam, Ind.	0–10	0.70
	10–30	0.79
Wabash silt loam, Nebr.	0–15	0.49
	15–36	0.56

itself: in the yellow and red earths of the south-central and southeastern states, which represent a transition from the podzol to the lateritic type of soil formation, we have an accumulation of TiO_2 in the surface soil. As we approach the Braunerde, the podzolic soils, there is a reversal in the TiO_2 content of the re-

spective surface and subsoil layers. This condition seems to prevail in the prairie soils, the degraded chernozems, of Indiana, Iowa, and Nebraska.

SUMMARY

Data are presented on the TiO_2 content of soils in the various parts of the world showing that the distribution of TiO_2 within the soil profile varies with the soil zones. It seems that in general the TiO_2 as an ampholyte behaves somewhat similarly to the R_2O_3 constituents. In the laterites the TiO_2 accumulates in the surface horizon. Similar tendencies are noted in the podzolic soils.

The mobility properties of TiO_2 have been inferred from studies on the isoelectric precipitation of TiO_2 in the hydroxide and phosphate system, following the methods inaugurated by Mattson. From the latter's work on the isoelectric precipitation in the R_2O_3 silicate and humate systems inference has been made on the behavior of TiO_2 in similar systems.

Data on the TiO_2 content in podzols and podzolic soils show that the TiO_2 is not mobile to any large extent. Comparisons of the TiO_2 content in the respective horizons in the profile bring out clearly that this constituent accumulates in the profile. Within the profile in the soils of the podzol zone there is an accumulation of TiO_2 in the B and sometime in the A_2 horizons. The probable reactions in the light of the isoelectric precipitation of TiO_2 in the lateritic and in the podzol process of soil formation are discussed.

Data are presented and discussed on the TiO_2 content in the colloid fractions of the surface soils and subsoils in several soil zones. It is brought out that in the zone of the yellow earths and red loams, the transition zone between the podzol and laterites, there is an accumulation of TiO_2 in the colloids of the surface soil, whereas in the podzolic and degraded chernozem zones there is an accumulation of TiO_2 in the colloids of the subsoil.

REFERENCES

(1) BENNETT, H. H., AND ALLISON, R. V. 1928 The Soils of Cuba. Tropical Plant Research Foundation, Washington, D. C.

(2) BLANCK, E. 1930 Die Mediterran-Roterde (terra rossa). *Blanck's Handbuch der Bodenlehre* 3: 194–257.

(3) BLANCK, E., AND GEILMANN, W. 1922 Etwas über die chemische Kennzeichnung des Tons und Kaolin. *Jour. Landw.* 70: 253–257.

(4) DUNNINGTON, F. P. 1891 Distribution of titanic oxide upon the surface of the earth. *Amer. Jour. Sci.* 42 (ser. 3) 491–495.

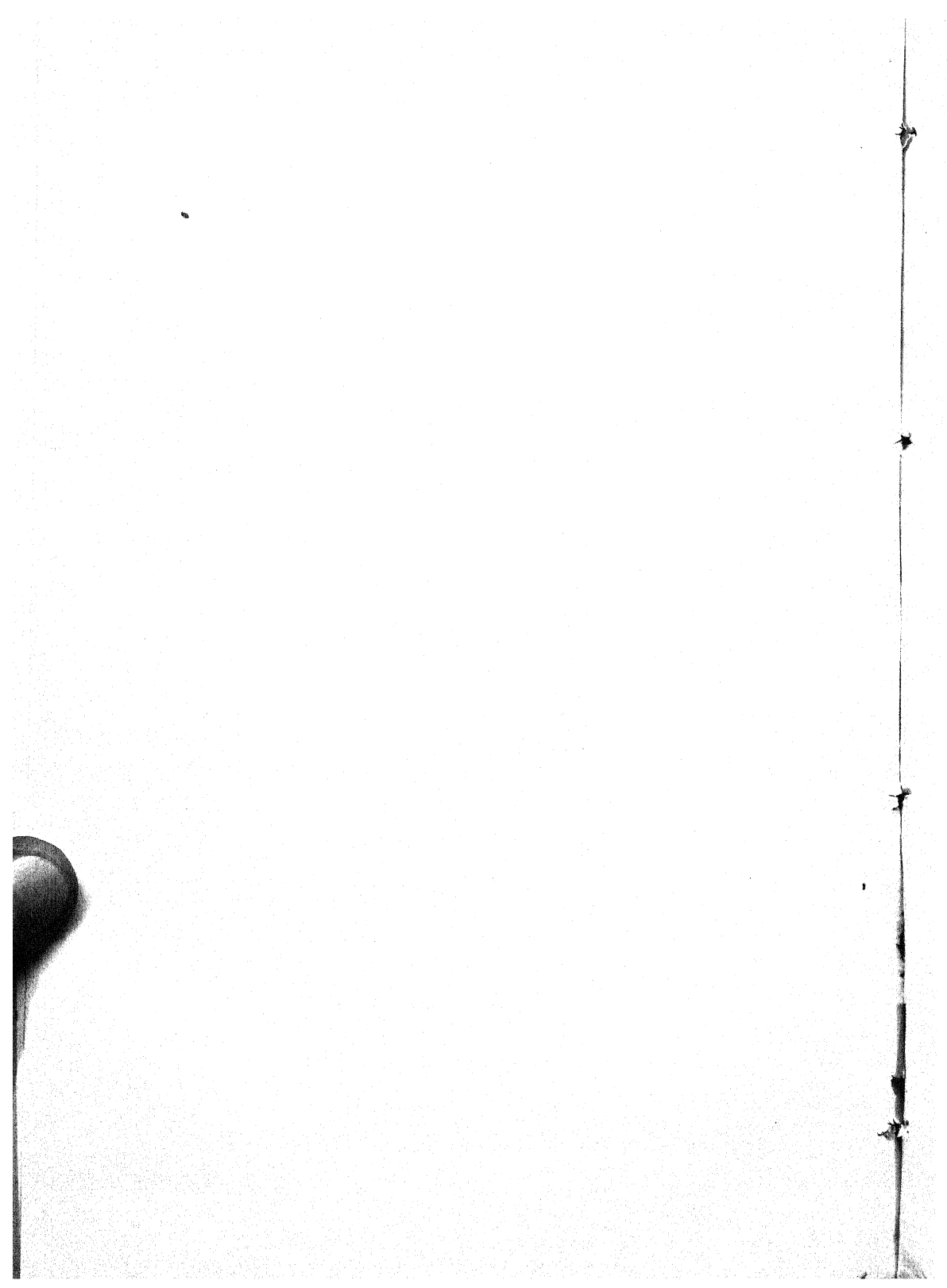
(5) GEILMANN, W. 1920 Über die Verbreitung des Titans in Böden und Pflanzen. *Jour. Landw.* 68: 107–124.

(6) HARRASSOWITZ, H. 1930 Böden der tropischen Regionen. *Blanck's Handbuch der Bodenlehre* 3: 362–436.

(7) JOFFE, J. S. 1932 Soil profile studies: IV. Morphological and chemical evidence of podzolization. *Soil Sci.* 33: 217–237.

(8) JOFFE, J. S. 1933 Morphology and genesis of podzols. *Amer. Soil Survey Assoc. Bul.* 14: 22–29.

(9) JOFFE, J. S., AND MCLEAN, H. C. 1928 Colloidal behavior of soils and soil fertility: IV. Anion effect on the precipitation reaction and degree of dispersion of Fe and Al hydroxides. *Soil Sci.* 26: 47–59.
(10) MCGEORGE, W. 1912 Soils. *Hawaii Agr. Exp. Sta. Ann. Rept.* 1912: 51–56.
(11) MARBUT, C. F. 1923 The soils of Africa. *Amer. Geog. Soc. Res. Ser.* 13: 115–221.
(12) MATTSON, S. 1928 Cataphoresis and the electrical neutralization of colloidal material. *Jour. Phys. Chem.* 32: 1532–1552. (See also *Jour. Phys. Chem.* (1933) 37: 223–227.)
(13) MATTSON, S. 1930 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459–495; IV. (1931) 31: 57–77.
(14) NIGGLI, P. 1926 Die chemische Gesteinverwitterung in der Schweiz. *Schweiz. Mineral. u. Petrograph. Mitt.* 5 (2): 222.
(15) PELLET, H., AND FREIBOURG, C. 1905 Titanium. *Ann. Sci. Agron.* 2 (ser. 10, II, No. 1): 20–84.
(16) ROBINSON, W. O. 1914 The inorganic compounds of some important American soils. U. S. Dept. Agr. Bul. 122.
(17) ROBINSON, W. O., AND HOLMES, R. S. 1924 The chemical composition of soil colloids. *U. S. Dept. Agr. Dept. Bul.* 1311: 1–41.
(18) STEINKOENIG, L. A. 1914 Distribution of certain constituents in the separates of loam soils. *Jour. Indus. and Engin. Chem.* 6: 576–577.
(19) STREMME, H. 1930 Die Braunerde. *Blanck's Handbuch der Bodenlehre* 3: 160–182.
(20) VERNADSKII, V. I. 1910 Titanium in soils. (Russian) *Pochvovedenie* (*Pedology*) 12: 255–259.



STUDIES ON SOIL PROTOZOA

F. S. BODENHEIMER AND K. REICH

Hebrew University, Jerusalem

Received for publication September 10, 1933

ANNUAL CYCLE OF SOIL PROTOZOA OF A POOR JERUSALEM SOIL

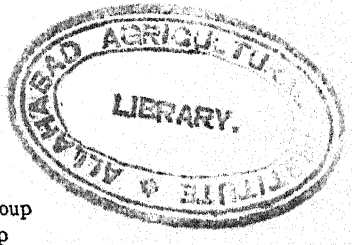
The observations were conducted in a wheat field on the western decline of Mount Scopus, near Jerusalem. The field was very shallow and had been worked primitively, without any manuring. The soil is described by Dr. A. Reifenberg as follows: "A yellow-brown, loamy lime-soil, which contains in considerable numbers undecomposed limestone fragments. The fine earth (particularly below 2 mm. diameter) contains 55.5 per cent $CaCO_3$. Its lime content is exceptionally high. The reaction of the soil is alkaline (pH = 7.5: colorimetric measurement). The soil contains dry plant remains, but no humus."

The technique of the present study was as follows: The soil was taken from the upper 5 cm., well mixed, and treated according to the method of Cutler (2) (dilution, cultivation in bouillon-agar, and hay infusion, etc.). The number of cysts was calculated by determining the difference between untreated soil and soil washed with 2 per cent HCl. The soil proved to be extremely poor in species of soil protozoa. The full list is (4):

Ciliata: *Colpoda steinii* Maup.

Flagellata: *Cercobodo* sp.
Heteromita globosa Stein
Pleuromonas jaculans Perty
Cercomonas longicauda Stein

Rhizopoda: *Mayorella palestinensis* Reich
Microamoeba oblonga Reich
3 *Amoebae* spp. of the *limax*-group
Amoeba sp. of the *proteus*-group



Sandon (6), who has studied the species of six different Palestine soils, obtained an average of 13.8 (8–31) species per soil. Our soil contained an average of 12.3 species. It should be noted, however, that two of our species occurred only very occasionally and that Sandon has studied only one sample of each soil. The distribution of the different groups, if we use the correction

factor set by Sandon (1.1 for Flagellata, 1.3 for Ciliata, 1.1 for Amoeba, 1.7 for testaceous Rhizopoda) is:

	CILIATA	FLAGELLATA	AMOEBA	TEST. RHIZOPODA	TOTAL
Sandon's average	3.7	6.4	2.4	0.6	13.1
Our Jerusalem soil	1.3	4.4	6.6	0.0	12.3
Difference	−2.4	−2.0	+4.2	−0.6	−0.8

But the average of the Palestine soils studied by Sandon was much influenced by the richness of his sample 8. The following is our comparison:

	CILIATA	FLAGELLATA	AMOEBA	TEST. RHIZOPODA
Best soil No. 8	6.7	14.3	6.0	3.6
Average of 5 other soils	3.3	4.8	1.7	0
Average of 3 poorest soils	1.9	4.2	1.8	0
Jerusalem soil	1.3	4.4	6.6	0

The differences as compared with our soil are relatively small. The number of Ciliata would have changed considerably had one other species only (as *C. cucullus* or *Oxytricha*) been present. The much higher standard with regard to *Amoeba* certainly constitutes no real difference, but is based on the fact that Sandon did not distinguish his species as well as we did, especially with regard to the *Amoeba limax* group. The annual fluctuation of the nine species, which appeared more or less regularly in the soil, is denoted in table 1.

The maximal active development for these species is:

	NOVEMBER	DECEMBER	JANUARY	FEBRUARY	MARCH	APRIL	MAY	JUNE	JULY	AUGUST	SEPTEMBER	OCTOBER
Number of species at maxima	1	1		3	3	3	1					
Per cent soil humidity (difference between fresh and dry soil)	12.2	7.1	12.1	11.1	11.8	12.3	4.3	4.3	1.5	2.2	1.0	2.2

It is obvious, therefore, that the winter rains start a period of activity, but only after a protracted period of soil saturation, and the rise of soil temperature in February induces the peak of this activity.

SOURCES OF ERROR IN PRESENT METHODS OF DETERMINING THE NUMBER OF CYSTS

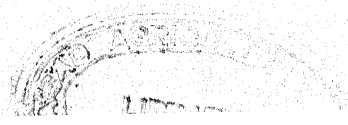
When we compare the number of active stages and of cysts in table 1, we are confronted by the startling fact that, except in two instances, *Mayorella*

TABLE 1

Number of active protozoa (a) and of cysts (b) for every month of the year per gram of the soil (dry weight)

		NOVEMBER 23, 1930	DECEMBER 5, 1930	JANUARY 6, 1931	FEBRUARY 5, 1931	MARCH 9, 1931	APRIL 13, 1931	MAY 3, 1931	JUNE 14, 1931	JULY 14, 1931	AUGUST 17, 1931	SEPTEMBER 19, 1931	OCTOBER 10, 1931
1. *Cercobodo* sp.	a	182	253	182	504	2034	730	166	82	282	112	323	459
	b	90	121	17	28	28	29	39	16	7	7		
2. *Heteromita globosa*	a	90	495	262	717	362	513	39	114	232	112	162	235
	b	63	42	7		28	17		7				
3. *Pleuromonas jaculans*	a	365	28	43	42	42	43	26				25	
	b	7	17				7						
4. *Cercomonas longicauda*	a	17	62	63	123	124	63		7	15	38	38	15
	b	17	28	17	28	7	7	7					
5. *Mayorella palestinensis*	a						17				7	7	
	b	17	352	262	717	42	17	39		111	80	7	235
6. *Microamoeba oblonga*	a				123	63	125	7	16	7	26	15	15
	b				62	16					7		
7. *Amoeba* No. 2	a						7						
	b				7		7						
8. *Amoeba* No. 4	a	7	42	17	7		17	16	16	7	7	7	15
	b												
9. *Amoeba x*	a				28	7	29	7			15	15	
	b					7							

palestinensis has more cysts than active forms. Our method was that actually used and proposed by Cutler (2). The soil is exposed to the influence of a 2 per cent solution of HCl overnight. It is supposed that at the end of this exposure, all active stages are dead, but no cysts damaged. This supposition is certainly not true, as the following experiments will show:



TREATMENT OF CULTURE	NUMBER OF INDIVIDUALS SURVIVING TREATMENT
1. Cercomonas longicauda	
I. Untreated control	15,200
II. 1.10 per cent HCl at 21°C	
III. 1.4 per cent HCl at 21°C	
IV. 1.8 per cent HCl at 21°C	
V. 2.0 per cent HCl at 21°C	
2. Cercomonas longicauda	
I. Untreated Control	72,000
II. 2 per cent HCl at 10°C	220
III. 2 per cent HCl at 16°C	76
IV. 2 per cent HCl at 22°C	50
3. Cercobodo sp.	
I. Untreated control	2,600
II. HCl 2 per cent at 11°C	
III. HCl 2 per cent at 15°C	
IV. HCl 2 per cent at 22°C	
4. Mayorella palestinensis Reich.	
I. HCl 2 per cent at 9.5°C	30,000
II. HCl 2 per cent at 16°C	15,000
III. HCl 2 per cent at 22°C	640

5. Soil sample

TREATMENT	NUMBER OF INDIVIDUALS SURVIVING				
	Cercobodo sp.	*Cercomonas longicauda*	*Heteromita globosa*	*Mayorella palestinensis*	*Amoeba* sp.
I. Untreated Control	1,300	38	1,800	6.8	167
II. HCl 2 per cent at 10°C	79	..	56	56	7
III. HCl 2 per cent at 24°C	56	..	38	15	..

It becomes obvious that the cysts of at least some of the soil protozoa become decidedly damaged by the treatment with HCl. The degree of this damage depends largely upon the prevailing environmental temperature, as is demonstrated in experiments 2 and 4. The value and applicability of the HCl method are thereby much restricted, and at higher temperatures the method is probably altogether valueless. Other methods (except the direct count) were unknown up to date, and we believe it impossible to draw from the relation between the numbers in active stages and the cysts (table 1) any conclusions whatsoever on the annual activity of the protozoa observed. With regard

to the very strange behavior of *Mayorella palestinensis*, we are not yet able to make a statement as to whether it is produced by direct stimulation of the cysts as a result of treatment with HCl, or whether it is attributable to the extermination of the bacteria in the culture medium (which have in other protozoa a well-known stimulative effect).

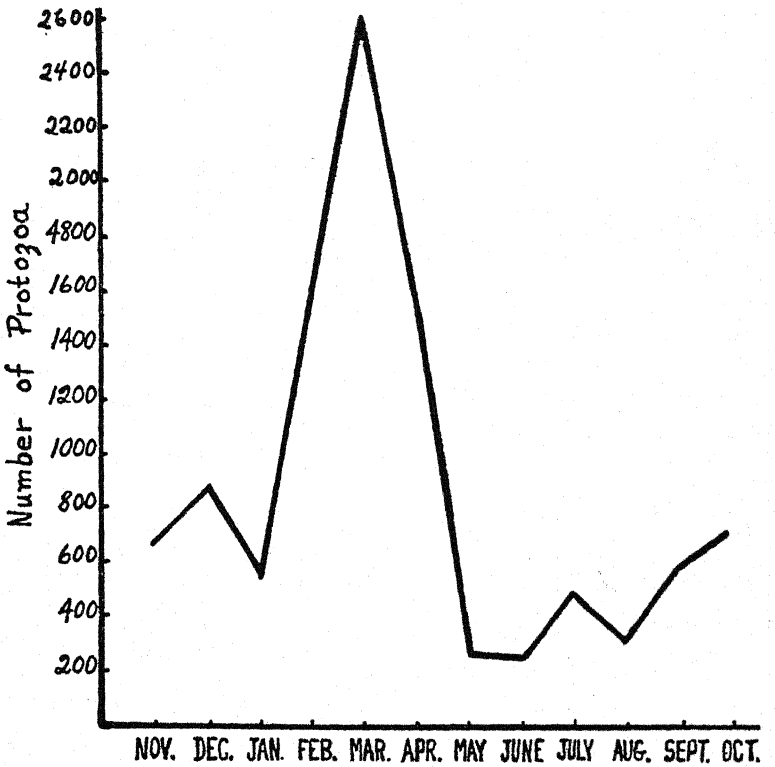


FIG. 1. NUMBER OF SOIL PROTOZOA

Sum of all individuals of all species during the year

UPPER LIMIT OF HEAT TOLERANCE IN THE CYSTS OF SOIL PROTOZOA

Some indications of the upper limit of heat tolerance in the cysts of soil protozoa (after exposure of 1 hour) may be found in the literature:

COUNTRY	AMOEBA	CILIATA	FLAGELLATA
	°C.	°C.	°C.
A. Egypt (3)	75–80	71–73	75–80
B. England (1)	72	72	70–72
C. England (5)	..	56	...

In samples A and B dry soil was tested, in sample C cysts from artificial cultures. Our own experiments explain this difference easily. Cysts in moist soil (our humid series) show a much lower tolerance than those from soil which was air-dried for more than 2 months.

TABLE 2

Upper limit of heat tolerance in the cysts of soil protozoa

TEMPERATURE	PROTOZOA ALIVE OR DEAD* AFTER EXPOSURE OF											
	Hours						Hours					
	1	2	3	4	5	6	1	2	3	4	5	6
°C.	Humid						Dry					
	Cercobodo sp.											
40			−	−	−	−						
45	−	−	+	+	+							
50	+	+	+	+			−	−	−	−	−	−
55	+						−	−	−	−	−	−
60	+		+				−	−	−	−	−	−
65							−	−	−	−	−	−
70							−	−	−	+	+	+
75			+				−	+	+	+	+	+
80							+	+	+	+	+	+
85							+	+	+	+	+	+
	Colpoda steinii											
40	−	−	−	−	−	−						
45	−	−	−	−	−	−						
50	−	+	+	+			−	−	−	−	−	−
55	−						−	−	−	−	−	−
60	+		+				−	−	−	−	−	−
65							−	−	−	−	−	−
70							−	−	−	−	−	−
75			+				−	−	+	+	+	+
80							+	+	+	+	+	+
85							+	+	+	+	+	+

TEMPERATURE	PROTOZOA ALIVE OR DEAD* AFTER EXPOSURE OF											
	Hours						Hours					
	1	2	3	4	5	6	1	2	3	4	5	6
°C.	Humid						Dry					
	Amoeba No. 2											
45						−						
50			−	−	−	−	−	−	−	−	−	−
55	−		−	−	+		−	−	−	−	−	−
60	−	−	+				−	−	−	−	−	−
65	+	+					−	−	−	−	−	−
70							−	−	−	−	−	−
75			+				−	−	+	+	+	+
80							+	+	+	+	+	+
	Mayorella palestinensis											
45						−						
50			−	−	−	−	−	−	−	−	−	−
55	−		+	+	+		−	−	−	−	−	−
60	−	−	−				−	−	−	−	−	−
65	+	+					−	−	−	−	−	−
70	+						−	−	−	−	−	−
75			+				−	−	−	−	−	−
80							−	+	+	+	+	+
90							+	+	+	+	+	+

* − = living; + = dead.

These results may be summed up as follows:

	UPPER HEAT TOLERANCE OF CYSTS IN	
	Humid Series	Dry Series
	°C.	°C.
Cercobodo sp.	50	80
Colpoda steinii	60	80
Mayorella palestinensis	65	85*
Amoeba No. 2	65	80

* Approximately.

This means that cysts may also show under different environmental conditions an entirely different tolerance for heat; the degree of dehydration of the cysts is especially important in this respect.

REFERENCES

(1) CUNNINGHAM, A., AND LÖHNIS, F. 1914 Studies on Soil protozoa; I. *Centrbl.* Bakt. (II) 39: 596–610.

(2) CUTLER, D. W. 1920 Method for estimating the number of active protozoa in the soil. *Jour. Agr. Sci.* 10: 135–143.

(3) MCKENZIE, TAYLOR E., AND BURNS, CHAMLEY, A. 1924 The effect of the summer fallow upon soil protozoa in Egypt. Egypt Min. Agr. Bul. 52.

(4) REICH, K. 1933 Studien über die Bodenprotozen Palästinas. *Arch. Protistenk.* 72: 76–98.

(5) RUSSELL, E. J., AND HUTCHINSON, H. B. 1913 The effect of partial sterilisation of soil on the production of plant food. *Jour. Agr. Sci.* 5: 188.

(6) SANDON, H. 1927 The Composition and Distribution of the Protozoan Fauna of the Soil. Edinburgh and London.

PROFILE STUDIES OF THE COASTAL PRAIRIE SOILS OF LOUISIANA: I. EXCHANGE AND SOLUTION PROPERTIES[1]

E. A. FIEGER AND M. B. STURGIS[2]

Louisiana State University

Received for publication October 16, 1933

The Coastal Prairie Area of southwest Louisiana and southeast Texas offers many unique problems for solution. Although some areas in this region have been mapped and the soils classified, no extensive laboratory investigations of these soils have been previously undertaken. This paper is the first of a series of studies of the morphology and genesis of the soils of this area and the effects produced upon the chemical, physical, and biological properties by current methods of agricultural practices.

In Louisiana the Coastal Prairie Area is situated in the extreme southwest corner of the state and extends northward from the Gulf of Mexico for a distance of 80 miles. It extends eastward from the Texas border about 125 miles. The area is small in comparison with the total area of the state, yet economically it is very important.

The soils of this area are relatively young, since the area only recently emerged from the Gulf of Mexico; the upper geological strata belong to the Port Hudson group of the Columbian Quarternary (6, 7). However, this does not mean that well-developed profiles are not in evidence, since sufficient time has elapsed for soil forming processes to cause such development. Natural drainage channels are poorly developed, and in conjunction with the flat topography and low elevation drainage is poor throughout the area. The rainfall is relatively high, averaging 53 inches per year, and the average temperature is likewise high, 68°F., with only a few killing frosts occurring in any year. The natural vegetation is grasses, although along the eastern and northern boundaries a transition belt of forest occurs. Because of the high rainfall, flat topography, and slow percolation of water through these soils, the cultivation of rice as the main agricultural crop has been developed. This crop, because of the irrigation or flooding of the soil required for its growth, has caused marked changes in the soil.

A study of these soils in the field has shown that the cultivation of rice has increased the stickyness, compactness, and imperviousness to the passage of water through the soil. At the present time the mechanism of these changes

[1] Published with the permission of the director of the Louisiana Agricultural Experiment Station and the dean of the College of Pure and Applied Science.

[2] Associate professor of chemistry and assistant soil technologist respectively.

in physical conditions of the soil is not entirely clear. It may be postulated that all of the following changes are instrumental in bringing this about:

1. Increased hydrolysis due to prolonged flooding with the liberation or solution of sodium ions, which have produced a partial sodium soil with the resultant change in physical properties.
2. Introduction of relatively high amounts of sodium ions in comparison with calcium and magnesium ions through the irrigating water, producing a condition similar to that resulting from such a case as the foregoing.
3. An increase in the dispersable colloid content of the soil due either to the direct effects of large amounts of water on the hydrolysis of the mineral content of the soil or to acceleration of hydrolysis by the ions present in solution.
4. The production of a highly reducing condition with the resultant solution and carrying to lower horizons of various elements, particularly iron and manganese.

All of these four factors will cause a change in the physical properties of the soil, in each case increasing the compactness and impermeability. The fate

TABLE 1

Analyses of water (6)

	LAKE CHARLES ARTESIAN WELL	INDIAN BAYOU	ENGLISH BAYOU
	p.p.m.	*p.p.m.*	*p.p.m.*
Calcium	21.0	15.0	11.0
Magnesium	8.0	11.0	3.0
Sodium	54.0	61.1	12.0
Potassium	30.0	30.0	6.0
Sulfate	10.0	26.0	4.0
Chloride	46.0	140.0	24.0
Bicarbonate	189.0	30.0	42.0

of the soil due to the introduction of sodium ions into the exchange complex will be similar to that taking place in arid regions, but will be less drastic, because of the lower concentration of the sodium ions present. Under the conditions that occur in Louisiana, where we have alternate years of flooding and fallow or cultivated crops, a high rainfall, and small quantities of sodium ions in the irrigating water, the saline or solonchak stage is transitory and would undoubtedly be in evidence only immediately after the removal of the saline irrigating water. In table 1 are given data on the analysis of water as reported by Heileman and Mesmer (7). During periods of drought, waters containing much higher amounts of soluble salts are sometimes used. Rice (12) reports such a condition for the summer of 1902 when great damage resulted from this cause. During such periods, when excessive quantities of water are used, the level of the water in the natural streams and bayous may become so low that saline waters from the Gulf of Mexico may back up to considerable distances and result in their becoming too saline for use on rice lands. As a result of the recurring saline conditions a weakly developed solonetz stage tends to be

formed. Dr. C. C. Nikiforoff states:[3] "Besides the typical solonetz there is a great group of soils alkalized to a lesser degree. The outstanding features of these soils are: chemical, some proportion of exchangeable sodium but relatively small; physical and morphological, compactness of the alkalized or solonized section of the profile. Such soils are much more common than the typical solonetz. They possess all the properties of the solonetz but in a smaller degree." There is associated with the effect of a lesser salinized condition upon the physical and chemical properties, the effect of restricted percolation which hinders the removal of the products of silicate weathering. As a consequence the weathering complex is more siliceous than where drainage is better (13). The accumulation of siliceous material and the existence of reducing conditions account for the gray colors and the pockets, stringers, or tongues of ashy degraded material in these soils. This is very much in evidence where a comparison is made between flooded and virgin soils. In all cases the irrigated soils show a much greater development of ashy siliceous material, and its occurrence is one of their outstanding characteristics.

The soil development in this region has taken place under rather sharply varying conditions The rainfall has been too high to permit the formation of a typical solonetz profile. Yet the original materials which contained calcareous shells, in passing through the tidal or saline marsh to the fresh water marsh and then to the low upland prairie with the recurrence from time to time of both natural and artificial floodings with saline waters, have left some profiles which in their older development are acid throughout, others which are younger or contained in the beginning more calcareous material and are acid only in the A horizon, and a few that do not occur widely, which are definitely alkaline. The movement of a great amount of rainfall as sheet water from the surface is a very important factor in the removal of salts from the soil. Following the emergence of the soil material from brackish water there was the rapid removal of soluble salts due to the heavy rainfall. Then, with the succession of grass flora, the occurrence of a definite alkaline stage was only transitory because of intense weathering by carbonation and hydrolysis associated with the quick removal of the soluble products from the surface horizon. This undoubtedly accounts for the ashy accumulations of siliceous pockets and tongues. The surface of the virgin soils are finely granular as a result of the relatively high accumulation of humus under grassland conditions, but under cropping and alternate flooding from irrigation, which causes the loss of organic matter, the soil becomes deflocculated. If at any time the irrigation waters contain salts there is a tendency toward a redevelopment of the alkaline stage which may be unnoticeable or very apparent depending upon the number of floodings and the concentration of salts in the water.

EXPERIMENTAL

Of the soils used in this study, two are from virgin fields and presumably have never been flooded; namely, soils 2 and 3; two have been flooded only with deep

[3] Mimeographed Lectures. University of Minnesota. 1929.

well water; namely, soils 1 and 6; and the others have been flooded at some previous time with saline water. A brief description of each profile follows:

Soil 1—Crowley silt loam, cultivated
- A 0–5½″ dark mouse gray, brown iron stains around channels of old roots, platy structure, irregular layer of dark, hard, round concretions at 4″ depth, mellow. Tongues or stringers of ashy gray material extend from this horizon to a depth of 20″.
- B_1 5½–15″ light gray streaked with brown silt loam, granular structure, compacted.
- B_2 15–23″ purplish brown clay, blocky, columnar, very compacted.
- C >23″ gray clay, mottled brown stains.

Soil 2—Crowley silt loam, virgin
- A 0–6″ dark gray, mellow, fine granular structure, no compaction. Ashy material much less than in soil 1.
- B 6–24″brownish gray silt loam, mellow, granular, slightly columnar.
- C >24″ gray clay mottled brown, small number of concretions.

Soil 3—Calcasieu fine sandy loam, virgin
- A 0–8″ yellowish brown, friable, slightly platy.
- B 8–17″ yellowish gray, very fine sandy loam, friable, brown concretions.
- C_1 17–27″ light yellowish gray silt loam, brown mottlings, concretions.
- C_2 >27″ grayish yellow, bright red mottlings, clay, iron concretions.

Soil 4—Lake Charles fine sandy loam, cultivated
- A 0–8″ dark mouse gray, slight brown mottlings, mellow, no compaction.
- B 8–20″ light yellow very fine sandy loam, dark brown and black concretions, compacted, beginning columnar development. On slight drying in field has appearance of salt incrustations on surface.
- C >20″ light olive gray clay, iron brown mottlings, breaks into blocky lumps.

Soil 5—Silt loam, cultivated
- A 0–6″ brownish black, horizontal platy structures, friable.
- B 6–27″ light gray, streaked with yellow and red mottlings, silty clay loam. Very sticky and compact, concoidal fracture, development of columns, surfaces of which are dark shiny gray.
- C >27″ mouse gray clay, lenses of very fine sand, yellow mottlings, brown and black concretions.

Soil 6—Silt loam, cultivated
- A 0–7″ dark brownish gray, friable.
- B 7–26″ dark gray silty clay loam, mottled with red and yellow, below 12″ from surface has ashy gray material occurring in tongues, pockets and coating soil particles. Where present in large amounts imparts mellowness to soil. Remainder is compacted and sticky and breaks into angular blocks and shows columnar development, has dark shiny surface.
- C >26″ olive gray clay, mottled, small brown and black concretions.

Soil 7—Lake Charles silty clay, cultivated.
- A 0–4″ dark gray, with brown mottlings, sticky.
- B 4–14″ grayish black heavy silt loam, tongues of grayish white extending to C. Small round concretions. Blocky structure with slight development of columns, very compacted.
- C >14″ yellow, mottled with bluish gray, clay. Lime concretions below 18″ from surface, few iron concretions above.

Soil 8—Lake Charles silt loam, cultivated
- A 0–8″ dark grayish black, mellow.
- B 8–21″ very dark mouse gray silt loam, granular structure, not compacted in

upper part, some compaction in lower part. Slight brown mottlings. Pockets of ashy material.

C >21″ light gray clay, few lime concretions.

In order to study the effect of the various previous floodings upon the chemical properties of the soil, the base exchange capacity and the concentration of the various bases in the exchange complex have been determined together with the hydrogen-ion concentration, total salt content, and soluble alkali.

For the determination of base exchange capacity normal neutral ammonium acetate solution was used as recommended by Schollenberger and Dreibelbis (14). Ten-gram samples were leached with 250 ml. solution in 10 ml. portions on Gooch crucibles by use of gentle suction. The excess ammonium acetate was washed from the soil with neutral ethyl alcohol (70 per cent). The adsorbed ammonium ion was determined by distillation with magnesium oxide as in the common procedure. In the leachate, aliquots of the leachate were used for determining the replaced bases. Calcium was precipitated as the oxalate, ignited, and weighed as the oxide. Magnesium was precipitated as magnesium ammonium phosphate and also determined gravimetrially. Sodium was precipitated from a separate aliquot and weighed as sodium magnesium uranyl acetate as recommended by Piper (10), and from a separate portion of the leachate potassium was precipitated and weighed as potassium sodium cobalti-nitrite (9, 15). The hydrogen-ion concentration was determined colorimetrically by using the soil itself as a filter in a perforated test tube percolator for obtaining a clear solution. Total salt content and soluble alkali were determined according to the method of the Association of Official Agricultural Chemists.

RESULTS AND DISCUSSION

As has been previously pointed out by Kelly and Brown (8), the substitution of sodium for the divalent bases produces two important effects; namely, first, the granular structure of the clay material becomes broken down with the resultant development of extreme impermeability; and, secondly, sodium carbonate is formed as a result of hydrolysis. Since the soils of the rice district have become extremely impermeable the question arose as to whether the impermeability was due to a substitution of sodium ions for divalent ions in the exchange complex. The results of base exchange studies on these soils show that this substitution has taken place to some extent. In table 2 is given a direct comparison of the base exchange values for a cultivated soil, No. 1, which has been flooded only with deep well water, and a virgin soil. Three distinct differences may be pointed out: the increase of exchangeable sodium in the A and the B horizons, the increase in alkalinity and pH value, and the increase in the total exchange capacity of the flooded soil in comparison to the virgin soil. The increase in the absolute amount of sodium in the complex in the A and B horizons averages approximately 100 per cent; however, the

relative increase is very slight—only 1 per cent and 1.5 per cent in the A and B horizons respectively when expressed on the basis of the per cent of sodium in the exchangeable bases. The increase in alkalinity in the A and B horizons indicates that the sodium may be in sufficient concentration to cause instability of the exchange complex with the resultant hydrolysis and production of small amounts of sodium hydroxide or carbonate (1, 4).

The marked increase in the total exchange capacity of the A and B horizons (table 2) is remarkable, since the organic matter has been reduced by cultivation to about one-half of that originally present, from 2.96 per cent to 1.68 per cent. This increase may be explained in one of two ways; namely, the hydrolysis of the mineral constituents of the soil resulting in the formation of substances which have a greater exchange capacity than that of the original minerals from which they were formed; or a change produced in the complex by the adsorbed sodium ions, changing it from the gel form to the sol form and

TABLE 2

Exchangeable bases in virgin and irrigated Crowley silt loam

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	*m.e.**	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
1-A	10.01	4.20	1.25	0.29	11.55	64	26	7.9	1.8	7.1	0.106	0.002
1-B_1	5.40	2.35	1.40	0.08	12.38	58	25	15	0.9	6.2	0.035	0.000
1-B_2	6.48	4.04	1.54	0.51	20.42	52	32	12	4.5	6.0	0.013	0.000
1-C	8.72	5.35	1.90	0.30	18.10	54	33	12	1.8	6.0	0.018	0.002
2-A	4.53	1.87	0.48	0.11	10.0	65	27	6.9	1.6	6.0	0.025	0.000
2-B	3.62	1.62	0.73	0.15	10.7	59	26	12	2.4	5.8	0.106	0.000
2-C	11.31	5.39	2.37	0.32	19.8	58	28	12	1.7	6.1	0.017	0.002

* Milligram equivalents per 100 gm. of dry soil.

thereby increasing the surface and causing through this the increased exchange capacity. Whether this increase is due directly to the hydrolytic action of water itself or is accelerated by the sodium ions present we are unable to state at present. It is interesting to note that the development of the so-called alkali areas require poor drainage as a primary prerequisite for their formation. This has been explained as being essential for the accumulation of soluble salts, principally sodium; for if the soluble salts are removed the complex becomes labile and an extremely compact, impermeable condition develops. Since this latter condition exists in the rice district of Louisiana, it appears that likewise an increase in total base exchange capacity should occur when alkali soils develop. Burgess has offered a possible explanation for this "build-up" in exchange capacity in the presence of increased alkalinity (2).

In the Coastal Prairie Area numerous dome-shaped mounds are found having an average height of 2 feet and a diameter of 16 to 50 feet or more.

These are characteristic topographic features of this region. In table 3 are presented the results of base exchange studies of a virgin mound, soil 3, and a cultivated mound, soil 4. Sample 4 was taken from a field which had been flooded with saline water in 1930. The results show that the saline treatment has materially increased the exchangeable sodium in the A horizon and increased it slightly in the B horizon. There has also been a slight increase in pH of the flooded soil in comparison with the virgin soil.

It is interesting to note that as early as 1901, Heileman and Mesmer (7) reported crop failures on mounds as being due to harmful salts present in them. They further state "The salts found in these soils [mounds] are such as commonly exist in alkali land. In all cases carbonates or black alkali are absent. . . . Alkali accumulation upon the area surveyed will never, perhaps, become a serious menace to the farmer." At the time their report was written the intimate connection between "white" and "black" alkali was not so perfectly

TABLE 3

Exchangeable bases in virgin and irrigated mounds

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
3-A	3.13	1.37	0.20	0.39	4.7	62	27	3.9	7.6	6.0	0.013	0.000
3-B	1.56	1.26	0.20	0.08	4.28	50	40	6.4	2.6	5.8	0.017	0.000
3-C_1	1.79	1.28	0.37	0.12	4.75	50	36	10.4	3.4	5.7	0.002	0.000
3-C_2	8.32	7.05	0.93	0.39	17.60	50	42	5.5	2.5	5.7	0.141	0.000
4-A	3.22	1.56	0.39	0.13	4.00	61	29.4	7.4	2.2	6.6	0.017	0.000
4-B	5.50	3.10	0.68	0.20	7.05	58	32.6	7.2	2.4	6.6	0.053	0.000
4-C	14.13	6.51	1.07	0.42	15.85	64	29	4.8	2.2	7.2	0.021	0.000

understood, and it is not surprising that they assumed that sodium carbonate would not be a menace. The most important point to consider is that the concentration of salt from irrigating waters was at that early date causing barren spots in rice fields. Through the courtesy of Mr. M. N. Stafford, we had occasion to visit some mounds which were barren of rice plants and which had black crusts or deposits upon their surfaces. An analysis of a representative sample from one of these mounds gave the following results: total salts 0.58 per cent, alkali carbonate 0.21 per cent, and soluble humus 0.22 per cent. This sample was taken within 6 miles of several samples reported by Heileman and Mesmer and shows here field evidence that sodium carbonate is being formed from the sodium salts present in the irrigating water as explained by Cummings and Kelley (4) and by Breazale and McGeorge (1). The water used for irrigating these fields was taken from Serpent Bayou and is not very different from the bayou waters reported in table 1. This emphasizes the importance of even small amounts of sodium in irrigating waters when such waters are used over long periods of time.

The effect of one recent flooding with highly saline water upon base exchange is shown in table 4. Soil 5 was flooded with saline water in 1930 at the time the rice crop was heading. The salt concentration was sufficiently high to kill all of the rice plants. In 1931 the field was fallowed, and in 1932 a poor yield of rice was obtained. Soil 6 has always been irrigated with deep well water and was taken from a field situated about one-fourth mile east of soil 5. Both soils are of recent origin, lying immediately north of the marsh fringing the Gulf Coast and have an elevation of 3 feet above the Gulf. It will be noted that

TABLE 4

Exchangeable bases in soils irrigated with fresh and salt water

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
5-A	6.28	2.91	1.31	0.26	8.75	59	27	12	2.5	6.9	0.074	0.004
5-B	19.76	8.00	4.20	0.56	17.60	61	25	13	1.5	7.3	0.071	0.006
5-C	18.01	8.31	3.06	0.47	17.60	60	28	10	1.5	7.6	0.045	0.013
6-A	9.12	2.72	1.10	0.07	8.60	70	21	8.4	0.5	7.1	0.134	0.002
6-B	13.27	6.55	1.22	0.25	13.40	62	31	5.7	1.2	6.8	0.406	0.000
6-C	23.60	10.33	1.50	0.24	18.70	66	29	4.2	0.7	7.5	0.025	0.009

TABLE 5

Exchangeable bases in soils of Lake Charles series which were irrigated with saline water

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
7-A	15.07	6.06	0.98	0.35	18.0	67	27	4.5	1.5	6.7	0.014	0.002
7-B	21.30	8.80	1.50	0.28	20.2	67	28	4.7	1.3	7.3	0.086	0.002
7-C	77.77	11.63	2.10	0.23	19.7	85	13	2.3	0.2	8.2	0.032	0.013
8-A	6.93	2.53	0.80	0.19	9.05	66	24	7.7	1.8	6.6	0.066	0.001
8-B	15.91	4.98	1.75	0.32	14.30	70	22	7.6	1.4	6.9	0.040	0.002
8-C	52.35	8.24	2.18	0.78	21.52	82	13	3.4	1.2	8.2	0.054	0.011

although there has been only a slight increase in the amount of exchangeable sodium in the A horizon, in the B and the C horizons the increase is very marked. This increased sodium content has materially increased the compactness, stickiness, and impermeability and has also increased the alkalinity of the soil. An increase in the exchange capacity in the B horizon of soil 5 is important as it indicates that sodium plays an important part in this phenomenon.

The study of base exchange upon two soils of the Lake Charles series is reported in table 5. Both these soils are giving poor yields and are highly

puddled and in poor physical condition, in spite of the fact that they are relatively high in organic matter. The amount of replaceable sodium, expressed in milliequivalents, is about the same as that for soil 1, but the per cent of sodium in the exchangeable bases is much less. Although the soils of the Lake Charles series contain more organic matter and more calcium than the soils of the Crowley series, apparently these two materials are only slightly effective in overcoming the effects of sodium upon the state of the soil, for soils 7 and 8 are only slightly more permeable than soil 1 and very much less than soil 2. In accordance with the results of other workers (3), it may be concluded that neither the absolute nor the relative amount of sodium in the exchangeable form can be used alone as an index for determining the physical condition of the soil.

Since the profiles of soils 6 and 7 had distinct pockets and stringers of gray material of ashy consistency, which are characteristic features of these soils, separate samples of this material were collected for further study from these

TABLE 6

Comparison of exchangeable bases of normal B with ashy degraded material

SOIL	Ca	Mg	Na	K	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE BASES				pH	SOLUBLE SALTS	ALKALI
						Ca	Mg	Na	K			
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*
7-B	21.30	8.80	1.50	0.28	20.2	67	28	4.7	1.3	7.3	0.086	0.002
7-D	16.72	7.32	1.47	0.29	15.8	65	28	5.7	1.3	7.2	0.246	0.001
6-B	13.27	6.55	1.22	0.25	13.40	62	31	5.7	1.2	6.8	0.406	0.001
6-D	9.07	4.07	0.98	0.12	8.55	64	29	6.9	0.8	6.9	0.251	0.002

profiles. The material collected had present considerable amounts of the compacted, darker colored material associated with it. In table 6 a comparison is made between this material, called D, and the normal B horizon from which it was taken. This degraded ashy material shows a much lower total base exchange capacity than the normal B, although the relative proportions of the various bases are very similar. In connection with the increase in the total exchange capacity which is due to the flooding of these soils, a material with a much lowered exchange capacity is present in the B horizon. Therefore, the values for increase in the B horizon do not represent the maximum increase of the compacted material, since all of the B samples contained varying amounts of the degraded material. It appears that this ashy gray material represents accumulation from both degradation of the complex and hydrolysis of the soil minerals and that there is represented here the change from a solonetz to a solodi or a similar change with the production of siliceous material and the removal of iron and aluminum. However, the change has not as yet progressed sufficiently to affect the fertility of these soils to a great extent.

Unless steps are taken to correct this condition we may expect the farmers on these soils to have increasing difficulty in producing profitable crops.

There are a number of references in the literature to the presence of salts in the irrigating waters used on the rice soils of Louisiana and Texas (5, 7, 11, 12). In all cases only the effect of the salt content upon the immediately growing rice crop is considered. Apparently the tacit assumption is made that the salts will be removed when the levees are opened and the fields drained at harvest time or will be removed by the following floodings with purer water or through leaching when the land is fallowed or in upland crop. In no cases are we aware that the effects of saline water upon the physical or chemical properties of these soils have been discussed or reported in the literature. The data presented here show that the waters used in flooding the Coastal Prairie soils have produced effects upon those properties. The small amounts of soluble alkali found should not be taken as an indication of only small changes in alkalinization, as Robinson (13) has pointed out that the percentage of sodium carbonate is no measure of this change and in the absence of carbon dioxide completely deflocculated soil may be formed without the presence of sodium carbonate. The changes induced by the monovalent cations in the irrigating water are analogous to those produced in other regions where irrigation is practiced.

SUMMARY

A study was made of the exchangeable bases in eight soil profiles of the Coastal Prairie Area of Louisiana. It included the evaluation of replaceable bases, base exchange capacity, H-ion concentration, total soluble salts, and soluble alkali. The soils were selected purposely for studying the effect of irrigating waters upon their chemical properties and changes of their physical state; two of the profiles were taken from virgin fields, two from fields which had been irrigated with deep well water, and the remainder from fields that had been irrigated at some previous time with saline water.

The irrigation of the soil caused an increase in the total exchange capacity and an increase in alkalinity. This may be due to the hydrolytic action of water itself, alone or in combination with monovalent basic ions. It appears that the hydrolytic effect is accentuated by the reducing conditions and lowered carbon dioxide production which follow from flooding and irrigation.

The use of saline irrigating water resulted in the greatest increase in the amount of replaceable sodium in the exchange complex, whereas deep well water caused the smallest increase, but in all cases flooding or irrigation caused an increase in comparison with non-flooded soils. The soluble alkali content was low, and in the case of the non-flooded soils no free alkali was present. In accordance with the work of others, it was found that there is no well-defined relationship between the amount or the proportion of exchangeable sodium and the impermeability of the soil to water. Excessive accumulations of soluble carbonate (black alkali) and other soluble salts account for the fact that some of the mounds in rice fields are bare.

The study of typical profiles has shown degradation extending from the A horizon well into the B horizon; the degraded material appears as a coating and is also concentrated in pockets, tongues, or stringers. This degraded material has resulted from the effect of the replacement of other ions in the exchange complex by sodium and also from the effects of reduction and hydrolysis on the mineral decomposition.

REFERENCES

(1) BREAZEALE, J. F., AND MCGEORGE, W. T. 1926 Sodium hydroxide rather than sodium carbonate the source of alkalinity in black alkali soils. Ariz. Agr. Exp. Sta. Tech. Bul. 13.

(2) BURGESS, P. S. 1929 The so-called "build-up" and "break-down" of soil zeolites as influenced by reaction. Ariz. Agr. Exp. Sta. Tech. Bul. 28.

(3) BURGESS, P. S., AND BREAZEALE, J. F. 1926 Methods for determining the replaceable bases of soils either in the presence or absence of alkali salts. Ariz. Agr. Exp. Sta. Tech. Bul. 9.

(4) CUMMINS, A. B., AND KELLEY, W. P. 1923 The formation of sodium carbonate in soils. Calif. Agr. Exp. Sta. Tech. Paper 3.

(5) FRAPS, G. S. 1927 The effect of salt water on rice. Tex. Agr. Exp. Sta. Bul. 371.

(6) HARRIS, G. D. 1902 Geological survey of Louisiana.

(7) HEILEMAN, W. H., AND MESMER, L. 1901 Soil survey of the Lake Charles area, Louisiana. U. S. Dept. Agr. Field Operations, Bureau of Soils.

(8) KELLEY, W. P., AND BROWN, S. M. 1924 Replaceable bases in soils. Calif. Agr. Exp. Sta. Tech. Paper 15.

(9) MORRIS, V. H., AND GERDEL, R. W. 1933 Rapid colorimetric determination of potassium in plant tissues. *Plant Physiol.* 8: 315–320.

(10) PIPER, C. S. 1932 The determination of sodium by precipitation as the triple salt sodium-uranyl-magnesium acetate. *Jour. Agr. Sci.* 22: 676–687.

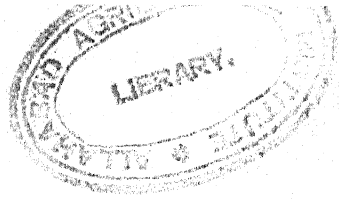
(11) QUEREAU, F. C. 1920 The amount of salt in irrigation water injurious to rice. La. Agr. Exp. Sta. Bul. 171.

(12) RICE, T. D., AND GRISWOLD, L. 1903 Soil survey of Acadia Parish, Louisiana. U: S. Dept. Agr. Field Operations, Bureau of Soils.

(13) ROBINSON, G. W. 1932 Soils: Their Origin, Constitution, and Classification. London.

(14) SCHOLLENBERGER, C. J., AND DREIBELBIS, F. R. 1930 Analytical methods in base exchange investigations on soils. *Soil Sci.* 30: 161–173.

(15) VAN RYSSELBERGE, P. J. 1931 Quantitative determination of potassium by sodium cobaltinitrite method. *Indus. and Engin. Chem.* (Anal. Ed.) 3: 3–4.



ANION EXCHANGE: II. LIBERATION OF THE PHOSPHORIC ACID IONS ADSORBED BY SOILS

S. RAVIKOVITCH

Jewish Agency Agricultural Experiment Station, Rehoboth, Palestine

Received for publication September 5, 1933

In part I of this paper it was established that the adsorption of phosphoric acid ions proceeds on the basis of an equivalent exchange with the exchangeable anions of the soil complex. The adsorbed phosphoric acid ions may reappear in the solution when they come in contact with other anions. The liberation of the PO_4 ions should proceed on the same principle of anion exchange reaction which took place when these ions entered the complex. The hydroxyl ions are the most effective anions in PO_4 replacement. By treating the soils with dilute solutions of acids, the greatest part of the adsorbed PO_4 is liberated in consequence of the destruction of the exchange complex by the acids. Together with the PO_4 ions, the products of the destroyed complex also appear in the solution. The anions, like SO_4 and Cl, are adsorbed by soils in very insignificant amounts (5, 8); they do not possess sufficient energy to replace anions like phosphoric acid, which are more strongly adsorbed. The liberation of the adsorbed PO_4, when the soils are treated with alkaline solutions of a low concentration, is due mainly to anion exchange reaction; the PO_4 is replaced by hydroxyl ions of the solutions.

The work presented herewith was undertaken to study the phenomenon of PO_4 liberation when soils containing phosphoric acid ions in adsorbed condition are brought in contact with Ca $(OH)_2$ and NaOH solutions, and to establish the rôle of the anions and cations of these solutions in the process of PO_4 liberation.

SOILS

The experiments were carried out with red sandy and Esdraelon clay soils. Phosphate ions were introduced into the H-soils by shaking the soils with H_3PO_4 solution of a low concentration, which yields the first form of adsorption for H-soils (part I). The excess of the unadsorbed PO_4 was removed by dialyzing through collodion bags. The difference between the amount of PO_4 in the soils after this treatment and its original amount in the soil gave the amount of adsorbed PO_4. The replacement of the exchangeable hydroxyls of the complex by the PO_4 ions was not complete, on account of the insufficient concentration of the PO_4 ions in the solution.

EXPERIMENTAL

The H-soil samples "saturated" with PO_4 were shaken with various quantities of $Ca(OH)_2$ or NaOH solutions. The soils together with the solutions were then transferred to dishes, evaporated, ground, and passed through a 1 mm. sieve. The prepared air-dry soil samples were transferred to small bottles with distilled water, the volume of water used being corrected for hygroscopic moisture so that the total volume was 50 cc. The soils were shaken for an hour and then left to settle for 4 days. After this period the soil extract was filtered and analyzed. The liberated PO_4 (2), the water-soluble Al_2O_3 (1),

TABLE 1

Effect of the addition of $Ca(OH)_2$ on the liberation of adsorbed PO_4 (a water extract of a H-sandy soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH CALCIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of $Ca(OH)_2$ added to the H-sandy soil sample*	Per cent of Ca introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0186	6.3	6.65
2	0.197	25.1	0.0108	3.6	6.75
3	0.393	50.0	0.0063	2.1	7.00
4	0.450	57.3	0.0055	1.9	7.00
5	0.489	62.2	0.0051	1.7	7.00
6	0.540	68.7	0.0063	2.1	7.00
7	0.590	75.0	0.0076	2.6	7.00
8	0.786	100.0	0.0104	3.5	7.05
9	0.807	102.8	0.0112	3.8	7.05
10	0.839	106.6	0.0117	4.0	7.05
11	0.892	113.5	0.0123	4.2	7.05
12	0.999	127.1	0.0144	4.9	7.05
13	1.106	140.7	0.0173	5.8	7.05

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-soil sample is 0.297 m.e.; the difference, therefore, between total anion exchange capacity and the adsorbed PO_4 ions is 0.489 m.e.

Fe_2O_3 (9), and SiO_2 (4a) were determined colorimetrically. All calculations were made on oven-dry weight.

CATIONIC AND ANIONIC EXCHANGE WHEN A $Ca(OH)_2$ SOLUTION IS ADDED TO THE SOIL

In series 1, to a range of 7.5-gm. samples of H-sandy soil containing PO_4 ions in adsorbed condition increasing amounts of $Ca(OH)_2$ were added. This was done to replace gradually the exchangeable hydrogen by Ca ions within the limits of the base exchange capacity of the complex. In certain experiments

the amount of added $Ca(OH)_2$ in milliequivalents surpassed the base exchange capacity of the complex established at pH 7.0. All the calcium in these experiments was completely adsorbed by the complex. The maximum of completely adsorbed calcium by a 7.5-gm. soil with an exchange capacity of 0.786 m.e. was 1.106 m.e. (table 1).

The completely unsaturated soil samples partly, as well as completely, saturated with calcium or with amounts of calcium surpassing the exchange capacity of the sample were shaken with distilled water. The amounts of PO_4 in the solution and the pH were determined.

In general, one may note that with the beginning of a gradual introduction of $Ca(OH)_2$ into the H-soil, the amount of PO_4 in the solution continuously de-

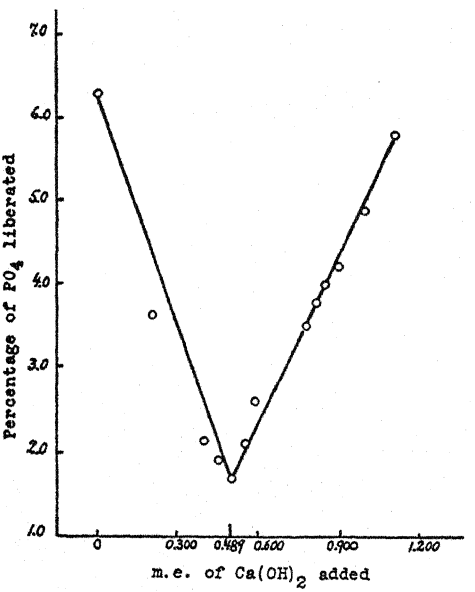


FIG. 1. EFFECT OF THE ADDITION OF $Ca(OH)_2$ ON THE LIBERATION OF PO_4 IN A H-SANDY SOIL

creases until it reaches a certain minimum. By its further introduction the amount of PO_4 begins to increase. This increase continues also when amounts of $Ca(OH)_2$ surpassing the exchange capacity of the soil sample are introduced. The characteristic feature of the curve of PO_4 liberation (fig. 1) is its preliminary descent followed by a sharp bend due to a sudden increase of the PO_4 in the solution. The first gradual decrease of the amount of the water-soluble PO_4 is due to the changes in the physicochemical state of the soil complex, brought about by replacement of its monovalent hydrogen ions with divalent calcium ions. As was found by Gedroiz (3, 4), the degree of dispersibility and of stability of the complex is dependent on the atomic weight and valence of its exchangeable cations. Mattson (6, 7) has established the dependence of the size of charge of the soil colloids, their degree of dispersibility

and swelling, and the dissociation of the adsorbed diffusible ions, on the kind of exchangeable cations. The degree of dispersibility and the dissociation of the adsorbed ions decrease, and the stability of connection between the components of the exchange complex increase when the exchangeable hydrogen is replaced by the divalent calcium. In the case of the less stable H-complex, the PO_4 passes into the solution in higher amounts than in the case of the same

TABLE 2

The degree of stability of the complex and the liberation of PO_4 as influenced by the various exchangeable cations (water extract)

EXPERIMENT NUMBER	MATERIAL FOR EXPERIMENTS	KIND OF CATION INTRODUCED INTO THE COMPLEX	Al IN 50 CC. OF THE EXTRACT	Fe IN 50 CC. OF THE EXTRACT	SiO_2 IN 50 CC. OF THE EXTRACT	PO_4 IN 50 CC. OF THE EXTRACT	pH
			m.e.	*m.e.*	*m.e.*	*m.e.*	
1	7.5 gm. of sandy soil con-	Ca	None	None	0.016	0.014	7.00
2	taining 0.189 m.e. of PO_4	H	0.014	Traces	0.042	0.021	6.65
3	in adsorbed condition	Na	0.014	0.005	0.038	0.076	7.25

TABLE 3

Effect of the addition of $Ca(OH)_2$ on the liberation of adsorbed PO_4 ions (a water extract of a H-sandy soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH CALCIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of $Ca(OH)_2$ added to the H-sandy soil sample*	Per cent of Ca introduced in relation to the total base exchange capacity			
			m.e.		
1	0.00	0.0	0.0205	10.9	6.65
2	0.20	25.4	0.0130	6.9	6.75
3	0.60	76.3	0.0093	4.9	7.00
4	0.65	82.7	0.0143	7.6	7.00
5	0.786	100.0	0.0186	9.9	7.05
6	1.106	140.7	0.0215	11.4	7.05

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-soil sample is 0.189 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 0.597 m.e.

complex saturated with calcium. The partial destruction of the H-complex causes a liberation of the PO_4 which was connected with it (table 2).

The limit of the decrease of the water-soluble PO_4 is attained when the amount of OH ions of the $Ca(OH)_2$ equals the amount of OH ions left in the complex after the PO_4 ions were introduced. The amount of the non-replaced exchangeable OH ions, calculated according to the difference between the total anion exchange capacity of the complex and the amount of adsorbed PO_4 ions,

equals 0.489 m.e. The action of the $Ca(OH)_2$ introduced in limits of 0.489 m.e. on the PO_4 liberation is entirely different from the action of that introduced beyond this limit. By its introduction into the soil within the limits indicated, only a cation exchange reaction proceeds between the Ca ions of the solution and the H ions of the complex which are in equilibrium with the OH ions. In connection with this cation exchange reaction those changes occur in the physicochemical properties of the complex which are responsible for the decrease of the liberated PO_4. With the introduction of $Ca^{++} \rightleftarrows 2OH^-$

TABLE 4

Effect of the addition of $Ca(OH)_2$ on the liberation of adsorbed PO_4 ions (a water extract of a H-clay soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH CALCIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of $Ca(OH)_2$ added to the H-soil sample*	Per cent of Ca introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0581	15.1	6.10
2	0.310	20.0	0.0465	12.1	6.50
3	0.619	40.0	0.0370	9.6	6.70
4	0.929	60.0	0.0317	8.3	6.75
5	1.120	72.4	0.0245	6.4	6.80
6	1.163	75.1	0.0237	6.2	6.85
7	1.238	80.0	0.0306	7.9	6.85
8	1.548	100.0	0.0401	10.4	7.05
9	1.648	106.5	0.0433	11.3	7.05
10	1.698	109.7	0.0465	12.1	7.05
11	1.798	116.2	0.0528	13.7	7.05
12	1.948	>116.2	0.0517	13.4	7.10
13	2.098	>116.2	0.0422	11.0	7.20
14	2.248	>116.2	0.0306	7.9	7.25
15	2.398	>116.2	0.0125	3.2	7.30

* The exchange capacity of the 3.0-gm. clay soil sample is 1.548 m.e.; the PO_4 adsorbed by the H-soil sample is 0.385 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 1.163 m.e.

ions into the H-soil in amounts surpassing the amount of the $OH^- \rightleftarrows H^+$ ions of the complex, an exchange reaction between the OH ions of the $Ca(OH)_2$ and the adsorbed PO_4 ions begins. This anion exchange proceeds simultaneously with the continuing cation adsorption.

In series 2 (table 3) the original soil material for the experiments is the same as in series 1 except that the amount of adsorbed PO_4 per 7.5-gm. sample is 0.189 m.e. The course of PO_4 liberation, as increasing amounts of $Ca(OH)_2$ are added, is entirely similar to that presented in the previous series of experiments.

The decrease of PO_4 in the solution occurs here, too, when $Ca(OH)_2$ is added in amounts which do not surpass in milliequivalents the amounts of the $OH^- \rightleftarrows H^+$ ions of the complex. When the amount of OH ions of the introduced $Ca(OH)_2$ surpasses in insignificant quantities the amount of OH ions of the complex, a sudden increase of PO_4 in the solution takes place.

In series 3 (table 4) a H-clay soil was used. With the addition of increasing amounts of $Ca(OH)_2$ to the H-soil sample, the amount of water-soluble PO_4 gradually decreases until it reaches its minimum, when 1.163 m.e. of $Ca(OH)_2$ is added. An insignificant addition of $Ca(OH)_2$ to the soil above this amount

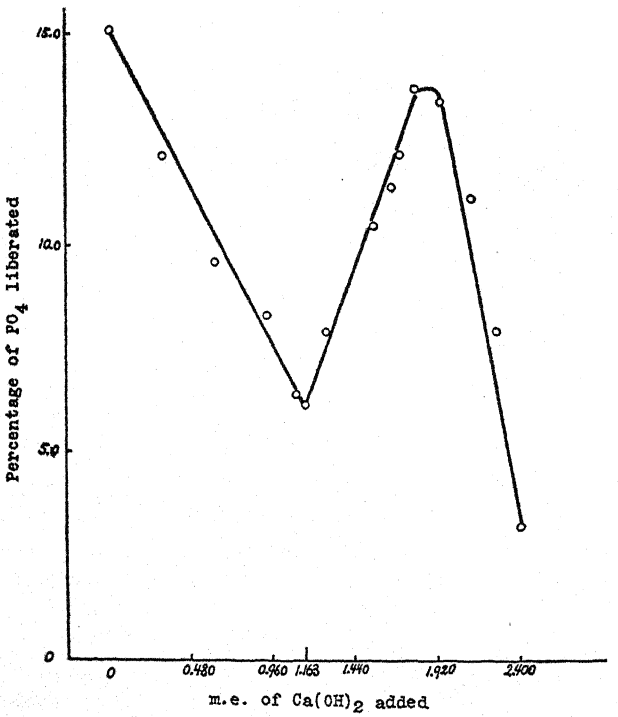


FIG. 2. EFFECT OF THE ADDITION OF $Ca(OH)_2$ ON THE LIBERATION OF PO_4 IN A H-CLAY SOIL

soon gives an increase of PO_4 in the solution. The curve of figure 2 begins to rise with the beginning of anion exchange. Here, too, as in the previous two series of experiments, this point is reached when the quantities of OH ions introduced by the $Ca(OH)_2$ solution exceed in an insignificant measure the amount of OH ions of the complex. The second bending of the curve, which represents the decrease in the amount of water-soluble PO_4, is due to the conversion of the liberated PO_4 into insoluble compounds as a result of introducing into the soil amounts of $Ca(OH)_2$ which cannot be completely adsorbed by it. The maximum amount of $Ca(OH)_2$ which is completely adsorbed by the sample of the clay soil is close to 1.95 m.e. Above this limit some $Ca(OH)_2$ is left in the solution as not adsorbed.

The adsorption of $Ca(OH)_2$ by a H-soil containing PO_4 ions in the exchange complex, in addition to its hydroxyls, proceeds in two phases. In the first place the Ca ions replace only the H ions of the complex which are in equilibrium with the hydroxyls; hence only a cationic exchange takes place. After replacement of all the exchangeable hydrogen ions which were in equilibrium with the OH ions and simultaneously with the continued adsorption of the cations, the anion exchange also begins. The OH ions of the $Ca(OH)_2$ begin to replace the adsorbed PO_4 ions. The phenomenon of replacement, in turn, of the exchangeable hydrogen can be explained by admitting a difference in the degree of dissociation of the $OH^- \rightleftarrows H^+$ ions and of the $PO_4^{\equiv} \rightleftarrows 3H^+$ ions of the complex. The degree of dissociation is probably higher in the first case, where the exchangeable anion is monovalent, than in the second case, where it is trivalent. The phenomenon of H replacement, in turn, can be explained also by the difference in degree of complexity of the exchange reaction, which is less complicated when it is only cationic, and more complicated when it is both anionic and cationic.

The replacement of the adsorbed PO_4 ions continues when amounts of $Ca(OH)_2$ which surpass the total base exchange capacity of the complex are added to the soil. This indicates that the complete exchange reaction between the adsorbed PO_4 ions and the introduced OH ions of the $Ca(OH)_2$ solution is not terminated, even after hydroxyls are added in sufficient quantities to produce a complete exchange of all the adsorbed PO_4 ions. It should be admitted that, in consequence of the more difficult exchange reaction between $PO_4^{\equiv} \rightleftarrows 3H^+$ ions of the complex and the $Ca^{++} + 2OH^-$ ions of the solution, simultaneously with the replacement of the PO_4 ions a part of the introduced $Ca(OH)_2$, without taking part in the exchange reaction, is adsorbed by the complex beyond its exchange capacity, established at pH 7.0.

The low amount of replaced PO_4 in the solution may be due to the secondary reactions which occur between the liberated PO_4 and the Ca(H)- complex, or between the PO_4 and the continuously introduced $Ca(OH)_2$.

The liberated PO_4 which appears in the solution in the form of H_3PO_4 and $Ca(H_2PO_4)_2$ is readsorbed according to the first form for Ca-soils. The readsorption of $Ca(H_2PO_4)_2$ should bring about the appearance of $Ca(OH)_2$ in the solution, which is probably being partly adsorbed by the complex and partly combined with the liberated PO_4, giving with it insoluble compounds.

CATIONIC AND ANIONIC EXCHANGE WHEN A NaOH SOLUTION IS ADDED TO THE H-SOILS

Series 4 and 5 (tables 5 and 6) indicate what influence may be exerted on the liberation of PO_4 by a partial or complete replacement of the exchangeable hydrogen by Na ions. The action of NaOH on the PO_4 liberation also is observed, when it is introduced in quantities which surpass the exchange capacity of the complex.

A different picture of PO_4 liberation is presented, in comparison with the

TABLE 5

Effect of the addition of NaOH on the liberation of adsorbed PO_4 ions (a water extract of a H-sandy soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH SODIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of NaOH added to the H-sandy soil sample*	Per cent of Na introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0190	6.40	6.65
2	0.197	25.1	0.0575	19.4	6.80
3	0.393	50.0	0.0575	19.4	7.0
4	0.450	57.3	0.0575	19.4	>7.0
5	0.489	62.2	0.0575	19.4	>7.0
6	0.540	68.7	0.0760	25.7	>7.0
7	0.786	100.0	0.0913	30.8	>7.0
8	0.865	>100.0	0.0997	33.6	>8.6

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-soil sample is 0.297 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 0.489 m.e.

TABLE 6

Effect of the addition of NaOH on the liberation of adsorbed PO_4 ions (a water extract of a H-clay soil)

EXPERIMENT NUMBER	DEGREE OF SATURATION OF THE H-SOIL COMPLEX WITH SODIUM		PO_4 FOUND IN 50 CC. OF THE EXTRACT	PERCENTAGE OF PO_4 LIBERATED	pH
	M.e. of NaOH added to the H-soil sample*	Per cent of Na introduced in relation to the total base exchange capacity			
			m.e.		
1	0.000	0.0	0.0581	15.1	6.10
2	0.310	20.0	0.0972	25.3	6.70
3	0.619	40.0	0.0972	25.3	6.90
4	0.929	60.0	0.0972	25.3	>7.0
5	1.120	72.4	0.0972	25.3	>7.0
6	1.163	75.1	0.0972	25.3	>7.0
7	1.238	80.0	0.1225	31.9	>7.0
8	1.548	100.0	0.1690	42.9	>7.0
9	1.703	>100.0	0.1817	47.2	>8.6

* The base exchange capacity of the 3.0-gm. clay soil sample is 1.548 m.e.; the PO_4 adsorbed by the H-soil sample is 0.385 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 1.163 m.e.

ones obtained, when the exchangeable hydrogen is replaced by Ca ions (figs. 3 and 4). As a certain amount of sodium is introduced into the H-complex the PO_4 in the solution increases at once. The amounts of liberated PO_4,

0.0575 m.e. for the sandy soil, and 0.0972 m.e. for the clay soil, are kept on a constant level until the OH ions of the NaOH are introduced in quantities which do not exceed those of the exchangeable hydroxyls left unreplaced by the PO_4 ions. When the OH ions are introduced into the soil in quantities

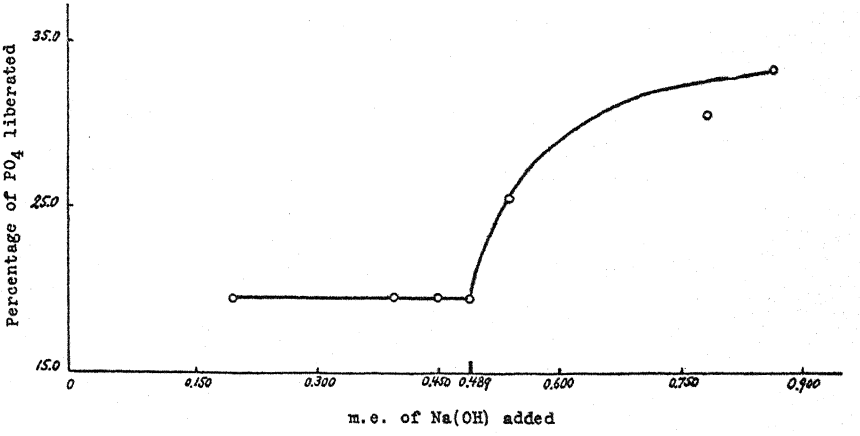


FIG. 3. EFFECT OF THE ADDITION OF NaOH ON THE LIBERATION OF PO_4 IN A H-SANDY SOIL

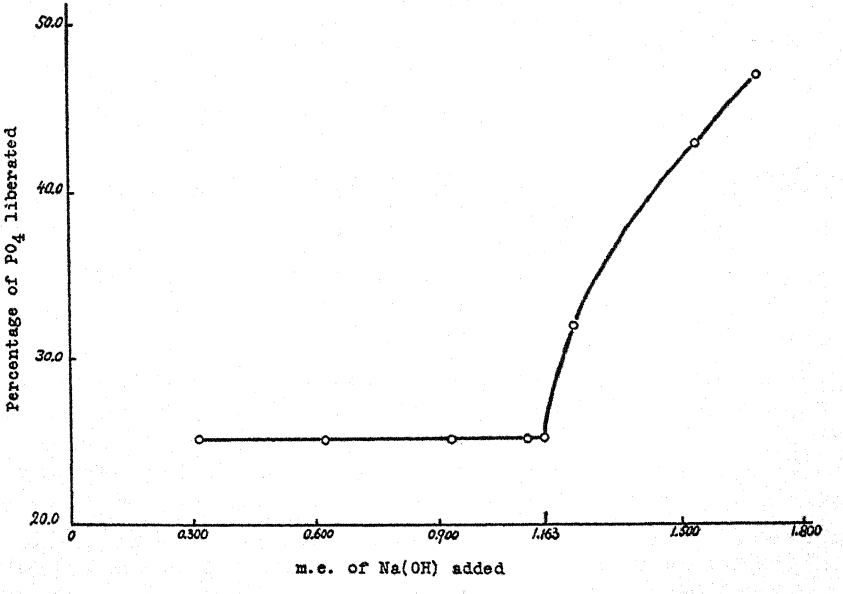


FIG. 4. EFFECT OF THE ADDITION OF NaOH ON THE LIBERATION OF PO_4 IN A H-CLAY SOIL

which surpass these limits only slightly, the amount of liberated PO_4 increases suddenly, as a result of the beginning of the anion exchange reaction, and this increase continues gradually with the further introduction of NaOH. Simultaneously with the anion exchange a continued cation exchange proceeds.

The presence of higher amounts of PO_4 in the solution as a result of the addition of NaOH, as compared with the amounts of PO_4 when similar quantities of $Ca(OH)_2$ are added, may be due: (*a*) to the increased dispersibility of the complex, its easier destruction, and the higher degree of dissociation of the diffusible ions when the complex contains Na instead of Ca ions (table 2); (*b*) to the lower readsorption of the liberated PO_4 by the Na-complex than by the Ca-complex.

The constant amount of PO_4 in the solution, when NaOH is introduced in quantities which cause a cation exchange reaction only, may be due to a finely established equilibrium between the liberated PO_4 and its different fixators, like the exchange complex and the aluminum and iron, the products of its destruction. With the starting of the anion exchange reaction the previously established equilibrium between the different fixators and the PO_4 is destroyed

TABLE 7

The partial destruction of the complex and the liberation of PO_4 as influenced by the addition of different quantities of NaOH to the H-soils (water extract)

EXPERIMENT NUMBER	NaOH ADDED TO THE H-SANDY SOIL SAMPLE*	Al IN 50 CC. OF THE EXTRACT	Fe IN 50 CC. OF THE EXTRACT	SiO_2 IN 50 CC. OF THE EXTRACT	PO_4 IN 50 CC. OF THE EXTRACT	pH
	m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
1	0.25	0.014	Traces		0.047	7.00
2	0.33	0.014	0.005	0.040	0.045	7.00
3	0.40	0.014	0.005	0.039	0.047	7.05
4	0.50	0.014	0.006	0.037	0.047	7.05
5	0.66	0.014	0.005	0.038	0.076	7.25
6	1.00	0.014	0.011	0.041	0.116	7.50

* The exchange capacity of the 7.5-gm. sandy soil sample is 0.786 m.e.; the PO_4 adsorbed by the H-sample is 0.189 m.e.; the difference, therefore, between the total anion exchange capacity and the adsorbed PO_4 ions is 0.597 m.e.

as a result of the appearance of increased amounts of replaced PO_4. The concentration of aluminum and iron present in the solution is almost constant (table 7).

The experiments of series 1 to 5 afforded an opportunity to verify the mechanism of the first form of adsorption according to which the PO_4 was fixed by the H-soil. As was stated in part I of this paper, an equivalent exchange between the hydroxyls of the complex and the trivalent PO_4 ions of the solution takes place in this form of adsorption. The correctness of this statement is confirmed by the results of the experiments in the present work, for the amount of exchangeable hydroxyls left unreplaced together with the amount of adsorbed phosphoric acid compose in milliequivalents exactly the total anion exchange capacity of the complex; that is, the adsorption of PO_4 proceeded on the principle of an equivalent exchange between the trivalent phosphoric acid ions and the hydroxyls of the soil complex.

EFFECT OF LIMING AND INTRODUCTION OF PHYSIOLOGICALLY ALKALINE SALTS INTO THE SOIL UPON THE LIBERATION OF ADSORBED PO_4

This study throws some light on the contradictory results obtained by different investigators regarding the liming of acid soils for the purpose of transforming the adsorbed PO_4 into an available form. The apparently contradictory phenomena in the process of PO_4 liberation which are observed when various acid soils are limed, take place also, as is shown in this work, when various quantities of $Ca(OH)_2$ are introduced into the very same unsaturated soil containing a definite amount of adsorbed PO_4.

The liming may have a favorable influence on the liberation of the adsorbed PO_4 when the exchangeable hydrogen ions which are in equilibrium with the hydroxyls are completely replaced, and when an excessive amount of $Ca(OH)_2$ is added. This excessive $Ca(OH)_2$ is needed for the replacement of the adsorbed PO_4. Part of the replaced PO_4 remains in the solution and part is readsorbed by the Ca-complex. The newly formed combination of PO_4 and Ca-complex, as will be seen in a later paper, is very unstable. As a result of hydrolysis of the exchangeable calcium which is in combination simultaneously with the adsorbed H_2PO_4 ion and with the exchange complex, or when this calcium is attacked by very weak acids, the aforementioned combination is broken up, causing the appearance of PO_4 in the solution.

The appearance of larger amounts of water-soluble PO_4 in the soil solution when physiologically alkaline fertilizers are introduced is the result of the action of the residual alkalinity on the exchange complex containing PO_4 in adsorbed condition. The basic ion, entering the complex, causes certain changes in the physicochemical state of the latter which favor the liberation of the PO_4. The adsorbed PO_4 may also be liberated by exchange with hydroxyls of the alkaline salts which may appear in the solution as a result of the introduction of physiologically alkaline fertilizers.

SUMMARY

The course of phosphoric acid liberation when $Ca(OH)_2$ or NaOH solutions are added to H-soils containing PO_4 ions in adsorbed condition, was studied. The influence of the exchangeable Ca, Na, and H ions on this liberation was considered.

In preparing the soil material for the study of PO_4 liberation, the trivalent phosphoric acid ions were introduced into the H-soils.

The exchange reactions, which begin as $Ca(OH)_2$ or NaOH solutions are added to the soil, proceed in two phases. In the first phase only a cationic exchange takes place between the Ca or the Na ions of the introduced solutions and the exchangeable H ions which are in equilibrium with the hydroxyl ions. As the replacement of these H ions is complete, the second phase of the exchange reactions proceeds. This exchange is anionic as well as cationic. It proceeds between the OH ions of the $Ca(OH)_2$ or NaOH solutions and the adsorbed PO_4 ions and, simultaneously, between the Ca or Na ions of the solutions and the exchangeable hydrogen ions which are in equilibrium with the adsorbed PO_4 ions.

The distribution of the reaction of hydrogen replacement into two phases can be explained by the difference in the degree of dissociation of the $OH^- \rightleftarrows H^+$ ions and of the $PO_4^{\equiv} \rightleftarrows 3H^+$ ions of the complex and the difference in the degree of complexity of the exchange reaction, which is in one case only cationic and in the other both anionic and cationic.

A gradual decrease in the amount of water-soluble PO_4 as the exchangeable hydrogen which is in equilibrium with the OH ions is gradually replaced by Ca ions, is directly related to the changes in the physicochemical state of the complex. The increase of PO_4 in the solution when additional amounts of $Ca(OH)_2$ are applied to the soil occurs with the beginning of PO_4 replacement. This anion exchange reaction takes place only when the quantity of OH ions introduced exceeds the quantity of OH ions which are present in the complex. The introduction of $Ca(OH)_2$ in amounts which can not be completely adsorbed by the soil causes a transformation of the liberated PO_4 into an insoluble condition.

The amount of PO_4 liberated is kept on an equal level as long as the introduced Na replaces only the exchangeable hydrogen ions which are in equilibrium with the OH ions. When NaOH is added in amounts of milliequivalents exceeding the amount of exchangeable OH ions of the complex, an anion exchange reaction begins between the additionally introduced OH ions and the adsorbed PO_4 ions.

The difference in the amount of liberated PO_4, when similar amounts of Ca or Na are introduced into the complex, is due to the differences in the degree of dispersion and stability of the calcium and sodium complexes and to the degree of dissociation of their diffusible ions.

The amount of PO_4 recovered in the solution, after all exchange reactions have taken place, appears to be the result of a final established equilibrium between the liberated PO_4, on one side, and the exchange complex, the products of its destruction, and the electrolytes of the solution, on the other.

REFERENCES

(1) ATACK, F. A. 1915 *Jour. Soc. Chem. Indus.* 34: 936.

(2) DENIGÉS, G. 1920 Reaction de coloration extrement sensible de phosphates et de arseniates. *Compt. Rend. Acad. Sci. (Paris)* 171: 802.

(3) GEDROIZ, K. K. 1924 Ultramechanical composition of soils and its dependence on the nature of the cations present in the soil in adsorbed condition. *Zhur. Opytn. Agr.* 22: 29.

(4) GEDROIZ, K. K. 1924 Soils unsaturated with bases. *Zhur. Opytn. Agr.* 22: 3.

(4a) GEDROIZ, K. K. 1923 The Chemical Analysis of Soils (Russian), p. 209.

(5) MATTSON, SANTE 1928 Anionic and cationic adsorption by soil colloidal materials of varying $\frac{SiO_2}{Al_2O_3 + Fe_2O_3}$ ratio. *Proc. and Papers First Internatl. Cong. Soil Sci. Comn.* II: 199–211.

(6) MATTSON, SANTE 1928 The influence of the exchangeable bases on the colloidal behavior of soil materials. *Proc. and Papers First Internatl. Cong. Soil Sci.*, p. 185.

(7) MATTSON, SANTE 1929 The laws of soil colloidal behavior: I. *Soil Sci.* 28: 179–220.

(8) MATTSON, SANTE 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 345–365.

(9) SHREINER, O., AND FAILYER, H. *U. S. Dept. Agr. Bur. Soils Bul.* 31: 38.

SORPTION OF LIQUIDS BY SOIL COLLOIDS: I. LIQUID INTAKE AND SWELLING BY SOIL COLLOIDAL MATERIALS

HANS WINTERKORN AND L. D. BAVER[1]

Missouri Agricultural Experiment Station[2]

Received for publication October 7, 1933

The present work was undertaken with the view of determining the factors governing the chemical melioration and stabilization of soils for agricultural and road building purposes. The experimental part of the study was designed with the following objectives in mind: (*a*) the development of a simple and accurate technic suitable for making routine analyses of the sorption of liquids by soils and soil colloids; (*b*) the formulating of a clearer conception of the physico-chemical properties of the colloidal clay particle in order to be able to predict with a higher degree of certainty the behavior of the soil under conditions of highway construction and agricultural manipulation; and (*c*) the obtaining of data which would be of value in critically examining the existing theories as to the mechanism of the swelling of soils and other colloidal systems.[3]

EXPERIMENTAL PRINCIPLES

When powdered soil colloids are placed in contact with a free water surface, water is taken up or sorbed. Although the exact nature of water sorption is not completely understood, the original assumption was made in this study that part of the water is taken up to fill the macro- and micro-pores and that the remaining sorbed amounts are used to produce the phenomenon of swelling. Since certain non-polar liquids such as benzene do not cause significant swelling when sorbed by soil colloids, they can be used to measure the pore space of the system. On the basis of these assumptions the amount of swelling water would be the difference between the sorbed amounts of water and benzene. Although it is realized that benzene may produce a small amount of swelling, that the size of the benzene molecule may prevent its entering all the pores that would sorb water, and that the total pore space in the presence of water

[1] Visiting assistant professor of chemistry and assistant professor of soils, respectively.

[2] Joint contribution from the Missouri State Highway Department and the University of Missouri, department of soils. Missouri Agricultural Experiment Station, Journal Series Paper No. 368.

[3] The data obtained will be analyzed in Part II from the point of view of (*a*) the thermodynamic treatment of Katz; (*b*) the Donnan membrane equilibrium as developed by Wilson, Procter, and Wilson and by Mattson; (*c*) the mechanistic, hydrodynamic treatment of Terzaghi; and (*d*) the concept of hydration and molecular orientation at surfaces and interfaces as instigated by the work of Hardy, Harkins, and Langmuir.

may be restricted somewhat by the swelling process, this method of measuring swelling offers an opportunity of obtaining valuable data concerning the behavior of soil colloids under conditions of water sorption.

The colloids, following their extraction, were electrodialyzed to form H-saturated systems thereby eliminating the variable factor of the nature of the adsorbed cation. From these H-systems, other cations were substituted on the surface of the colloid by adding the respective hydroxides. They were air-dried and ground to pass a 300-mesh screen in order to minimize the effect of particle size. They were then dried in a desiccator over P_2O_5. This method of drying was chosen in order to avoid any irreversible changes as a result of heating the colloid. The moisture content was reduced almost to the same value as in oven drying.

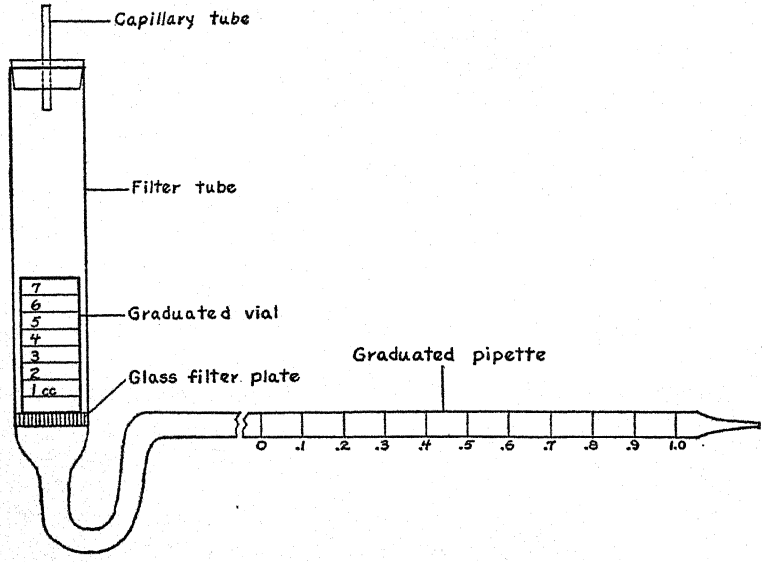


FIG. 1. APPARATUS FOR MEASURING THE LIQUID SORPTION AND SWELLING OF SOIL COLLOIDS

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus used in this study was constructed upon the principle of measuring the intake of liquid by powdered colloids through a porous plate and avoiding a positive or negative pressure head of the liquid. It so happened that in its final form it resembled quite closely the Freundlich apparatus (3) which was devised independently about the same time. The apparatus most frequently used (fig. 1) consists of a Jena glass tube with a fused-in sintered-glass filter disc; the Jena tube was connected to a microburette by a small glass tube. The microburette had a capacity of 1 cc. and could be read to 0.002 cc. When the swelling of bentonite was measured, a three-way stopcock connected to a water reservoir was inserted between the Jena glass tube

and the microburette. Such a connection permitted the introduction of more water as sorption progressed. Liquids which dissolve or attack stopcock grease cannot be used with the stopcock connection, however.

A weighed amount of powdered colloid, usually 0.5 gm., was poured into a calibrated glass tube, 1 cm. in diameter and 2 cm. long, closed at the bottom with a fine silk cloth; the colloid was lightly packed with a glass pestle. This tube was placed upon the moist filter disc in the apparatus; the apparatus was then closed with a rubber stopper. A glass capillary through the stopper and another at the end of the burette provided equal pressures at both surfaces of the sorption liquid, and at the same time rendered negligible the loss from evaporation. Measurements were made in an air thermostat maintained at a temperature of 30°C. The liquid intake was determined by reading the burette at different time intervals. Most of the experiments could be terminated after 24 hours, since this time was usually sufficient for the saturation of the system with the liquids in question. Duplicate determinations could be made to check within a deviation of from 2 to 5 per cent. The simplicity and accuracy of the technic render it most adaptable to routine laboratory analyses.

Since the sorption of liquids is intimately related to surface phenomena, the amount of sorption should be expected to vary with the nature of the sorbing surface and the properties of the sorbed liquid. In order to obtain data that would shed some light on these surface reactions experiments were so designed as to employ (*a*) colloids of varied chemical constitution both as to their crystal lattice compositions and as to the nature of the ions adsorbed upon the colloidal surfaces, and (*b*) liquids possessing a wide range in their dielectric properties but maintaining a certain similarity in their molecular structures.

The following colloids, extracted from widely different soils and electrodialyzed, were used in this study:

1. Cecil colloid from the subsoil of a clay loam from Alabama. SiO_2-sesquioxide ratio, 1.3.
2. Susquehanna colloid from the well-oxidized horizon of the Susquehanna clay from Alabama. SiO_2-sesquioxide ratio, 2.3.
3. Putnam colloid from the heavy layer of a silt loam from Missouri. SiO_2-sesquioxide ratio, 3.2.
4. Wabash colloid from an alluvial clay from Missouri. SiO_2-sesquioxide ratio, 3.2.
5. Lufkin colloid from the surface layer of a Black Belt soil from Alabama. SiO_2-sesquioxide ratio, 3.8.
6. Bentonite, a colloidal fraction from commercial Wyoming bentonite. SiO_2-sesquioxide ratio, 5.0.

The different liquids employed were: distilled water; absolute methyl, ethyl, propyl, and amyl alcohols; carbon tetrachloride; benzene; toluene; xylene; aniline; and nitrobenzene. The alcohols were purified by boiling with calcium oxide and subsequent distillation; the other liquids by repeated distillation.

EXPERIMENTAL RESULTS

The size of secondary particles and sorption of liquids. In order to determine what effect the fineness of grinding the dry colloidal material has upon the

sorption of liquids, the Putnam colloid was ground to give three different sizes of particles: (*a*) particles smaller than 0.053 mm. in diameter, (*b*) particles ranging from 0.053 to 0.10 mm., and (*c*) particles ranging from 0.10 to 0.25 mm. The intake of both water and benzene was studied, and the results are shown in table 1. The rate of water sorption during the first few minutes was rather rapid after which it decreased to almost zero at the end of 24 hours. This rapid intake of water during the early stages of the experiment is primarily the result of filling the capillary pores. Benzene sorption was complete after 5 minutes, indicating that all the available capillaries had been filled. When the

TABLE 1

The relationship between water intake and size of the secondary particle of the soil colloid

TIME	WATER INTAKE BY 0.5 GM. OF COLLOID					
	(*a*)*		(*b*)		(*c*)	
minutes	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*	*cc.*
1	0.571	0.675	0.615	0.622	0.602	0.583
2	0.656	0.705	0.645	0.645	0.617	0.610
3	0.681	0.715	0.655	0.655	0.625	0.618
4	0.691	0.725	0.660	0.662	0.629	0.623
5	0.701	0.730	0.665	0.667	0.632	0.625
10	0.724	0.750	0.680	0.680	0.645	0.640
20	0.746	0.768	0.691	0.693	0.654	0.650
30	0.761	0.777	0.698	0.700	0.660	0.657
60	0.781	0.792	0.711	0.713	0.672	0.667
120	0.800	0.809	0.726	0.729	0.687	0.680
1,200	0.858	0.864	0.779	0.789	0.750	0.737
1,260	0.859	0.864	0.780	0.791	0.753	0.740
1,380	0.865	0.867	0.784	0.797	0.760	0.746
1,440	0.867	0.868	0.785	0.799		
1,660	0.871	0.870	0.789	0.803	0.767	0.754
2,640	0.898	0.893	0.815	0.831	0.802	0.787
2,820	0.901	0.894	0.819	0.836	0.806	0.790

* (*a*) Particles smaller than 0.053 mm.
(*b*) Particles from 0.053 to 0.10 mm.
(*c*) Particles from 0.10 to 0.25 mm.

sorbed amount of benzene is subtracted from the sorbed water to obtain the swelling water it is seen that the swelling of particles with diameters less than 0.10 mm. is practically the same. The particles larger than 0.10 mm. seemingly show the largest swelling. This is probably due to a dispersion effect of the water. On the basis of these data colloids were ground to give particles smaller than 0.1 mm. in cases where only comparative values were desired. In all other experiments they were smaller than 0.05 mm.

The effect of dielectric constant and molecular structure on the sorption of liquids. If swelling is a phenomenon associated with the electrical field forces on the surface of the colloidal particles, it should also be expected to be a function of

the electrical properties of the liquid. Consequently, there should be a correlation between the sorption of a liquid by powdered soil colloids and the dielectric constant of the liquid. The different attempts of other investigators to connect dielectric constants with swelling will be discussed later.

The data obtained in this study are given in tables 2 and 3. Table 2 shows the relationship between the dielectric constant and sorption when more or less non-polar liquids are used. In table 3 the correlation between sorption and

TABLE 2

*The intake of non-polar liquids and dielectric constants**

LIQUID	INTAKE	DIELECTRIC CONSTANT
	cc.	
CCl_4	0.318	2.22
Benzene	0.318	2.26
Toluene	0.323	2.36
Xylene	0.324	2.48
Aniline	0.356	7.00
Nitrobenzene	0.373	34.30

* Particle size <0.1 mm.

TABLE 3

*The sorption of polar liquids and dielectric constant**

LIQUID	INTAKE	DIELECTRIC CONSTANT D	SWELLING S	D/S
	cc.			
H-OH	0.99	76.0	0.58	131
H_3C-OH	0.66	31.9	0.25	128
H_5C_2-OH	0.60	24.1	0.19	127
H_7C_3-OH	0.57	20.5	0.16	128
$H_{11}C_5$-OH	0.53	14.6	0.12	122
Pore space CCl_4	0.41	2.2		...

* Particle size <0.053 mm.

swelling and the dielectric constant of water and various alcohols is shown. Both sets of data indicate that a relationship between swelling and the dielectric properties of the liquid exists only if there is a certain similarity in the molecular structure of the liquids. The data in table 3 show that the swelling of colloids in consequence of the sorption of a polar liquid of the water type may be expressed more or less quantitatively by the equation

$$\frac{L - P}{L' - P} = k \frac{D}{D'}$$

Where L = cc. of sorbed liquid with dielectric constant, D.
L' = cc. of sorbed liquid with dielectric constant, D'.
P = cc. of pore space as measured with a non-swelling liquid.
k = constant.

Since the structural similarity of the molecules in different liquids or the similarity of their electric fields is, according to Harkins (4), expressed by their

TABLE 4

Water intake as a function of the SiO_2-sesquioxide ratio

COLLOID	INTAKE	PORE SPACE	SWELLING	SiO_2/R_2O_3	BASE EXCHANGE CAPACITY, M.E. PER 100 GM.
	*cc.**	*cc.**	*cc.**		
H-Cecil	0.655	0.620	0.035	1.3	13
H-Susquehanna	0.830	0.550	0.280	2.3	47
H-Putnam	0.870	0.390	0.480	3.2	65
H-Wabash†	0.920	0.450	0.470	3.2	78
H-Lufkin	0.990	0.410	0.580	3.8	82
H-Bentonite	1.885	0.725	1.160	5.0	95

* Per 0.5 gm. colloid. Sorption of water by all colloids except bentonite was practically complete after 24 hours; bentonite intake required 7 days.

† Relatively high content of organic colloid influences sorption considerably.

TABLE 5

Water intake by Putnam colloid saturated with different cations

CATION	INTAKE*	PORE SPACE	SWELLING
	cc.†	*cc.*†	*cc.*†
Li	3.250	0.625	2.625
Na	2.725	0.625	2.100
K	0.733	0.480	0.253
Ba	0.873	0.450	0.423
Ca	0.954	0.500	0.454
H	0.900	0.490	0.410

* The end readings for K-, Ba-, Ca-, and H-colloids were taken after 24 hours, and those for the Li- and Na-colloids after 56 hours. The values for Li- and Na-colloids are somewhat too low as a result of diffusion of the highly dispersed colloid through the filter plate.

† Per 0.5 gm. colloid.

miscibilities, the values for D/S in table 3 should be expected to deviate from that for water with decreasing solubility of the alcohols in water; this is their actual behavior. It may be emphasized that because of the experimental definition of "swelling" as used in this investigation, the aforementioned formula can at present be looked upon only as a semi-quantitative expression of the swelling of soil colloids in liquids with a field structure similar to that of water.

Influence of the nature of the colloidal surface on water sorption. It has been shown by Baver (2), Mattson (6), Freundlich (3), and others that the chemical composition of the colloid (crystal lattice structure determined by the SiO_2-sesquioxide ratio of the colloid) and the nature of the adsorbed ions influence such physicochemical properties as viscosity, plasticity, and volume changes. Freundlich, Mattson, Anderson (1), Woodman and Chapman (7), Joseph and Oakley (5), and others have demonstrated a certain apparent functional correlation between water absorption and the nature of the colloidal particle. These data, however, do not permit a complete discussion of the various factors involved, since the nature of the adsorbed ions and their effects on water sorption were not extensively studied. Inasmuch as various colloids with different crystal lattices and saturated with various ions were studied somewhat in detail in this investigation with regard to water sorption and swelling, considerable data have been accumulated which promise to shed some light on the nature of the swelling process. A complete discussion of the data obtained will be reserved for Part II of this study; it will suffice at this time to mention briefly a few of the typical results obtained. The data in table 4 show that water sorption and swelling increase with the SiO_2-sesquioxide ratio of the colloid, indicating that sorption is correlated with the constitution of the alumino-silicate responsible for the properties of the colloid. The data in table 5 indicate vividly that the nature of the adsorbed ion plays a distinct part in the phenomenon of water sorption. It is especially striking that the H-, Ba-, and Ca-ions should be similar in their behavior and that the K-ion should have such a repressing effect upon the water intake of these colloidal systems. These relationships are specific for colloids other than the Putnam colloid. Their theoretical and practical significance will be discussed later.

SUMMARY

A simple method for measuring the liquid intake and the swelling of soils and soil colloids is described.

The sorption of various liquids by powdered soil colloids was measured. It was found that swelling, defined as the difference between sorption of swelling liquid and intake of non-swelling liquid, is a function of form and intensity of the electric field around the liquid molecules. The swelling of soil colloids in liquids having a water-like structure, as related to the dielectric constant, is expressed by a simple formula.

The influence of the SiO_2-sesquioxide ratio and the nature of the adsorbed cation was studied.

REFERENCES

(1) ANDERSON, M. S. 1929 The influence of substituted cations on the properties of soil colloids. *Jour. Agr. Res.* 38: 565–584.

(2) BAVER, L. D. 1929 The effect of the amount and nature of exchangeable cations on the structure of colloidal clay. Missouri Agr. Exp. Sta. Res. Bul. 129.

(3) FREUNDLICH, H., SCHMIDT, O., AND LINDAU, G. 1932 Ueber die Thixotropie der Bentonite-suspensionen. *Kolloidchem. Beihefte* 36: 43–81.

(4) HARKINS, W. D. 1926 Surface energy and surface tension. *Colloid Chemistry* by Jerome Alexander 1: 192–264.

(5) JOSEPH, A. F., AND OAKLEY, M. B. 1929 The properties of heavy alkaline soils containing different exchangeable bases. *Jour. Agr. Sci.* 19: 121–131.

(6) MATTSON, S. 1927 The influence of the exchangeable bases on the colloidal behavior of soil materials. *Proc. First Internatl. Soil Cong.* 2: 185–198.

(7) WOODMAN, R. M., AND CHAPMAN, G. M. 1932 The behavior of clay gels under small pressure, and the influence of the exchangeable bases present. *Jour. Soc. Chem. Indus. Trans.* 51: 175–178.

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XIV. THE ELECTROKINETICS OF HYDROUS OXIDES AND THEIR IONIC EXCHANGE[1]

SANTE MATTSON[2] AND A. J. PUGH

New Jersey Agricultural Experiment Station

Received for publication September 12, 1933

When a solution of a metallic salt such as the chlorides of tin, ferric iron, and aluminum is treated with alkali there is formed a voluminous gelatinous precipitate called "hydroxide," to which a definite formula $X \cdot OH_y$ is usually assigned. These compounds have long been known to be colloidal in nature, and usually the hydrous oxides formed by treating with water or dilute alkali carry a positive charge. It was very early recognized that the hydroxides thus formed carry some of the anion in a form that is difficult to remove by dialysis through a semi-permeable membrane, although many attempts have been made to obtain a "pure colloid."

Under the ordinary conditions of preparation, that is by dialysis of an easily hydrolyzed salt such as the acetate, nitrates, or chlorides, the sols of a series of hydroxides, such as aluminum, ferric, zinc, and copper hydroxides, are always positively charged. Powis (4), however, working with the preparation of colloidal ferric hydroxide, showed that the sign of the charge is a matter of ionic environment during the preparation. Colloidal ferric hydroxide prepared by dialysis of the chloride is positively charged, which is attributed by Powis to a preferential adsorption of the ferric ion, which is present in excess. This ion is preferentially adsorbed by the colloid particle, and confers its positive charge on the colloidal micells. By allowing a dilute solution of ferric chloride to run slowly to a slight excess of dilute alkali hydroxide, Powis succeeded in preparing a negatively charged ferric hydroxide. The negative charge of the resulting sol in this case is attributed to a preferential adsorption of the hydroxyl ion from the alkaline solution.

Mattson (1) in a series of investigations has shown that the charge of a large number of colloidal materials is a function of the pH in the dispersion medium

[1] Editor's Note: It will be noted that this paper bears the same serial number (XIV) as the paper by A. J. Pugh published in the May 1934 issue of SOIL SCIENCE (vol. 37, no. 5, p. 403). The paper by Pugh and a subsequent one entitled "Laws of Soil Colloidal Behavior: XV. Ionic Exchange with Hydroxides," which appeared in the August 1934 issue of SOIL SCIENCE (vol. 38, no. 2, p. 161), are not part of Mattson's series and should be numbered papers I and II of Pugh's series "Laws of Soil Colloidal Behavior."

Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

[2] Now at the College of Agriculture, Uppsala, Sweden.

and of the nature of the anions in combination. The colloids investigated included a great many different materials, such as the hydroxides of iron and aluminum, phosphates, silicates, humates, and the colloidal material that is present in the soil. All of these precipitates fall into a large class of substances, and may be defined as colloidal ampholytes, the main factor governing the sign of the charge being the pH of the external medium. In order to understand the processes as it affects other hydroxides the work has been extended in this paper to include the hydroxides of other metals, which can be isoelectrically precipitated.

EXPERIMENTAL METHOD

The method employed for preparing the compound for a determination of the isoelectric point, is the same as has previously been employed by one of us. Measured portions of a dilute solution of the salt of the metal were placed in a

TABLE 120

The $Yt(NO_3)_3$ + NaOH system

A. 10 m.e. $Yt(NO_3)_3$ in 1,000 cc.

B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.4	Clear	Clear		7.9
20	1.5	Clear	Clear		
20	1.6	Rapid	xxxx	Slow +	8.9
20	1.7	Rapid	xxxx	Slow −	9.0
20	1.8	Rapid	xxxx	−0.7	9.2
20	1.9	Rapid	xxxx	−1.2	9.5
20	2.3	Rapid	xxxx	−2.0	10.7
20	3.0	Rapid	xxxx	−2.7	11.0

Plus water to make total volume 50 cc. Isoelectric pH 8.95.

beaker, and the pH range at which maximum flocculation occurred was obtained by a preliminary titration with sodium hydroxide. A series of precipitates were then prepared to cover this range, the pH being adjusted at short intervals by NaOH in progressively increasing quantities, the total volume in each case being made up to 50 cc. The flocculation after mixing, and after standing overnight is recorded in the tables, x representing slight flocculation, xx about half complete, xxx nearly complete, and xxxx complete flocculation. The flocs were allowed to stand overnight, the pH of the supernatant liquid and the cataphoresis measurements were made in the manner previously described.

THE ISOELECTRIC POINT

In previous publications by Mattson and Parberry and by Mattson the isoelectric precipitation of aluminum and ferric hydroxides (1, III), stannous

hydroxide, and antimony oxychloride (3) has been discussed. In this work we have studied the precipitation of hydroxides by NaOH from the following salts: $Yt(NO_3)_3$, $LaCl_3$, $TiCl_4$, $Zr(NO_3)_4$, $CeCl_4$, $Th(NO_3)_4$, $SnCl_4$, $Pb(NO_3)_2$, $ZnCl_2$, $MgCl_2$, $CoCl_2$, and $NiCl_2$.[3] The results are shown in tables 120–130.

The precipitates flocculate rapidly at the isoelectric point as well as over a certain range on either side of this point. Beyond this zone of rapid flocculation more or less stable sols are usually formed, especially in dilute solutions.

TABLE 121

The $LaCl_3$ + NaOH system

A. 10 m.e. $LaCl_3$ in 1,000 cc.
B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.5	Clear	Clear		8.2
20	1.7	Clear	Clear		8.2
20	1.8	Clear	xxxx	+1.5	9.2
20	1.9	Clear	xxxx	+0.9	10.3
20	2.0	Rapid	xxxx	±0.0	10.4
20	2.3	Rapid	xxxx	−0.7	10.9
20	2.9	Rapid	xxxx	−1.5	11.1
20	3.2	Rapid	xxxx	−2.0	11.5
20	3.5	Rapid	xxxx	−v. slow	11.6

Plus water to make total volume 50 cc. Isoelectric pH 10.4.

By direct observation or by interpolation we find the following order for the isoelectric pH as far as investigated:

Isoelectric pH of various hydroxides

	HYDROXIDE												
	Sn(ic)	Ti(ic)	Sb	Sn(ous)	Zr	Ce	Th	Fe(ic)	Al	Yt	Zn	La	Pb
Isoelectric pH.....	3.9	4.8	5.6	6.6	6.7	6.75	6.85	7.1	8.1	8.95	10.3	10.4	11.0

Two hydroxides, Mg and Ni, remained electropositive up to pH 12.0, whereas Co appeared to be practically isoelectric at pH 11.4. Although no high degree of accuracy can be claimed for these values, since it is extremely difficult to measure the movements of gelatinous flocs, it is evident that there exists a general relationship between the isoelectric point of the hydroxides and the

[3] In the absence of non-polarizable electrodes it is not possible to determine the charge of the precipitates at pH values above 12.0 or below 3.0, because of the evolution of gas at the electrodes, which causes a displacement of the liquid within the cell.

position the metals occupy in the periodic system. Thus the isoelectric pH increases with the metallic and electropositive character as we pass from a lower to a higher atomic weight within a group of elements. The trivalent elements, Al, Yt, and La, give isoelectric hydroxides at pH 8.1, 8.95, and 10.4

TABLE 122

The $TiCl_4$ + NaOH system

A. 10 m.e. $TiCl_4$ in 1,000 cc.
B. 50 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	7.0	Opal	xx	+3.0	3.6
20	7.8	Opal	xxx	+3.0	4.0
20	8.0	Slow	xxxx	+3.0	4.1
20	8.2	Rapid	xxxx	+1.2	4.6
20	8.4	Instant	xxxx	+0.6	4.6
20	8.5	Instant	xxxx	−1.2	5.0
20	8.6	Rapid	xxxx	−2.7	6.4
20	8.8	Slow	xxx	−3.0	6.7
20	9.0	Opal	xxx	−3.0	7.4

Plus water to make total volume 50 cc. Isoelectric pH 4.8.

TABLE 123

The $Zr(NO_3)_4$ + NaOH system

A. 10 m.e. $Zr(NO_3)_4$ in 1,000 cc.
B. 10 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	8.0	Clear	Clear		5.4
20	9.0	Instant	xxxx	+3.0	6.2
20	9.5	Instant	xxxx	+3.0	6.5
20	9.75	Instant	xxxx	+2.5	6.5
20	10.0	Instant	xxxx	+1.7	6.5
20	10.25	Clear	xx	−2.7	7.0
20	10.5	Clear	x		7.1
20	11.0	Clear	Clear		8.6

Plus water to make total volume 50 cc. Isoelectric pH 6.7.

respectively. The same applies to the tetravalent elements in the fourth group, Ti, Zr, Ce, and Th, although the difference between the latter three is very small. Cerium, which in the normal form is trivalent, was oxidized to the tetravalent form by the addition of a few drops of hydrogen peroxide before precipitation.

The isoelectric pH values decrease, therefore, with an increase in the acid properties of the elements. Those elements which form hydroxides having a high isoelectric pH occur among the first groups in the periodic system, whereas the more acidic elements have a lower isoelectric pH. The elements in the center of the system yield hydrous oxides isoelectric near the point of neutrality.

TABLE 124

The $CeCl_4$ + NaOH system

A. 10 m.e. $CeCl_4$ in 1,000 cc.
B. 20 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	2.0	Clear	Clear		
20	4.0	Clear	xx	+3.0	
20	5.0	Opal	xx	+2.5	
20	5.2	Instant	xxxx	+0.7	6.4
20	5.5	Instant	xxxx	−0.7	7.1
20	5.7	Instant	xxxx	−1.0	8.0
20	6.5	Instant	xxxx	−3.0	9.8
20	8.0	Opal	xxxx	−3.8	10.2

Isoelectric at pH 6.75.

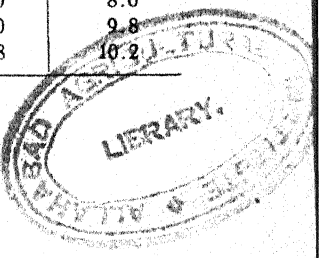


TABLE 125

The $Th(NO_3)_4$ + NaOH system

A. 10 m.e. $Th(NO_3)_4$ in 1,000 cc.
B. 10 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	14	Clear	xx	+1.5	6.2
20	15	Slow	xxx	+0.5	6.8
20	16	Instant	xxxx	−1.5	7.0
20	17	Instant	xxxx	−2.9	9.2
20	18	Rapid	xxxx	−3.0	9.8
20	19	Rapid	xxx	−3.0	10.0

Plus water to make total volume 50 cc. Isoelectric pH 6.85.

There are, however, irregularities in the electrokinetics of the hydrous oxides just as there are irregularities in the periodicity of the chemical properties of the elements. Thus, according to unpublished data by Hester and Mattson, copper in the first group and manganese in the seventh group yield, when $CuCl_2$ and $MnCl_2$ are precipitated by NaOH, hydroxides isoelectric at pH 7.6 and 7.05 respectively. These elements differ markedly also in their chemical

properties from the neighboring elements in the periodic system. The cataphoretic isoelectric point does not always express the acidic and basic properties that would be expected from the position of the elements in the periodic table, for reasons that will be discussed later.

TABLE 126

The $SnCl_4$ + NaOH system

A. 10 m.e. $SnCl_4$ in 1,000 cc.

B. 50 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	0.2	Instant	xxxx	+1.8	3.2
20	1.0	Instant	xxxx	+1.8	3.2
20	1.4	Instant	xxxx	+1.8	3.3
20	1.8	Instant	xxxx	+1.3	3.4
20	2.0	Instant	xxxx	+1.3	3.4
20	2.2	Instant	xxxx	+slow	3.5
20	2.5	Instant	xxxx	±0.0	3.9
20	3.0	Opal	x	−1.8	6.4

Plus water to make total volume 50 cc. Isoelectric pH 3.9.

TABLE 127

The $Pb(NO_3)_2$ + NaOH system

A. 10 m.e. $Pb(NO_3)_2$ in 1,000 cc.

B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	2.0	Rapid	xxxx	+1.5	9.4
20	2.5	Rapid	xxxx	+1.0	11.0
20	3.5	Instant	xxxx	+0.6	11.0
20	3.6	Instant	xxxx	−0.5	11.0
20	3.7	Instant	xxxx	−0.8	11.1
20	3.9	Instant	xxxx	−0.8	11.2
20	4.5	Slow	xxxx	−slow	12.0

Plus water to make total volume 50 cc. Isoelectric pH 11.0.

Cation adsorption and exchange

The hydroxides of stannic and stannous tin, titanium, aluminum, and ferric iron were prepared in bulk by precipitation from a normal solution of their respective chlorides at the isoelectric pH. They were removed from the mother liquor by filtration, but without washing, and to facilitate the work

TABLE 128

The $ZnCl_2$ + NaOH system

A. 10 m.e. $ZnCl_2$ in 1,000 cc.

B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.0	Clear	xxxx	+2.9	6.5
20	1.5	Slow	xxxx	+1.5	6.8
20	2.0	Instant	xxxx	+1.0	9.6
20	2.1	Instant	xxxx	±0.0	10.3
20	2.2	Instant	xxxx	−slow	10.3
20	2.4	Clear	xxxx	−0.3	11.0
20	3.0	Clear	x		12.0

Plus water to make total volume of 50 cc. Isoelectric pH 10.3.

TABLE 129

The $MgCl_2$ + NaOH system

A. 10 m.e. $MgCl_2$ in 1,000 cc.

B. 100 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	3.0	Opal	xxxx	+1.5	9.6
20	3.5	Opal	xxxx	+1.5	9.6
20	4.5	Opal	xxxx	+1.5	10.0
20	5.0	Opal	xxxx	+1.4	10.9
20	10.0	Opal	xxxx	+slow	12.0

Plus water to make up to 50 cc. Isoelectric pH undetermined.

TABLE 130

The $CoCl_2$ + NaOH system

A. 10 m.e. $CoCl_2$ in 1,000 cc.

B. 50 m.e. NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1/VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	1.5	Opal	xxxx	+2.0	8.0
20	2.0	Slow	xxxx	+1.5	8.2
20	3.0	Rapid	xxxx	+1.5	8.2
20	4.0	Rapid	xxxx	+1.5	9.2
20	5.0	Rapid	xxxx	+0.5	10.6
20	6.0	Rapid	xxxx	±slow	11.4
20	6.5	Rapid	xxxx	±slow	11.6

Plus water to make total volume 50 cc.

TABLE 131

Cation adsorption and exchange by isoelectrically precipitated hydroxides

HYDROUS OXIDES	ISOELECTRIC pH	EXCHANGEABLE Ba, M.E. PER GRAM AT pH 7	EXCHANGEABLE Ba, M.E. PER GRAM AT ISOELECTRIC pH OF COLLOID
Stannic	3.9	1.01	0.00
Titanium	4.8	0.84	0.00
Stannous	6.6	0.21	
Ferric	7.1	0.00	0.00
Aluminum	8.1	0.00	0.00

TABLE 132

Adsorption of the oxalate ion by isoelectrically precipitated hydroxides

(Milliequivalents C_2O_4 per 0.5 gm. colloid)

HYDROXIDE	pH AT EQUILIBRIUM	C_2O_4 ADDED	C_2O_4 IN SUPERNATANT LIQUID	C_2O_4 ADSORBED
		m.e.	*m.e.*	*m.e.*
Ferric	6.0	1.70	1.167	0.533
	6.7	1.70	1.290	0.410
	7.1	1.70	1.352	0.348
	8.4	1.70	1.495	0.205
	8.8	1.70	1.546	0.154
	8.9	1.70	1.659	0.041
Aluminum	4.5	1.70	1.310	0.390
	7.2	1.70	1.284	0.416
	7.4	1.70	1.342	0.358
	8.2	1.70	1.361	0.339
	8.4	1.70	1.403	0.297
	8.7	1.70	1.485	0.215
	9.0	1.70	1.485	0.215
	9.2	1.70	1.536	0.164
Titanium	3.2	1.70	1.147	0.553
	6.6	1.70	1.454	0.246
	8.0	1.70	1.514	0.184
	8.2	1.70	1.556	0.144
Stannic	3.2	1.70	1.361	0.339
	3.6	1.70	1.413	0.289
	4.8	1.70	1.597	0.103
	8.6	1.70	1.699	0.001
Magnesium	9.4	1.70	1.680	0.020
	9.6	1.70	1.700	
	9.8	1.70	1.700	

they were dried at 65°C., and powdered. Their base exchange was determined at pH 7, and also at the isoelectric pH, by leaching with Ba-acetate until the pH of the leachate was equal to the pH of the original Ba-acetate solution. When the base exchange is determined with Ba-acetate at a pH corresponding to the isoelectric pH of the compound, the equilibrium is established immediately, but in order to make the two determinations comparable the leaching was continued until about 250 cc. of the solution had passed through the filter. Then 10 cc. of *N* $BaCl_2$ solution was added to the filter, and the compound washed free of chlorine. The adsorbed barium was displaced with hot *N*

TABLE 133

Adsorption of sulfate ion by isoelectrically precipitated hydroxides

(0.5 gm. colloid)

ISOELECTRIC HYDROXIDE	pH AT EQUILIBRIUM	SO_4 ADDED	SO_4 IN SUPERNATANT LIQUID	SO_4 ADSORBED
		m.e.	*m.e.*	*m.e.*
Magnesium	9.3	1.72	1.72	
	9.5	1.72	1.72	
	9.6	1.72	1.72	
Ferric	3.3	1.72	1.08	0.64
	3.4	1.72	1.15	0.57
	4.0	1.72	1.24	0.48
	7.1	1.72	1.52	0.20
	7.2	1.72	1.52	0.20
Aluminum	4.2	1.72	1.23	0.49
	4.2	1.72	1.15	0.57
	4.4	1.72	1.23	0.49
	4.8	1.72	1.28	0.44
	6.8	1.72	1.34	0.38

NH_4Cl and the barium estimated gravimetrically as sulfate. The results are given in table 131.

The data demonstrate quite conclusively that those hydroxides that are isoelectric on the acid side of the neutral point possess the power to adsorb and exchange cations at pH 7.0, and that this capacity is greater the lower the isoelectric pH. Both tin and titanium hydroxide have an extremely high base exchange capacity, which is of the same order of magnitude as the various soil colloids and the amphoteric silicates, phosphates, and humates, having the corresponding isoelectric points (1, III). Aluminum and ferric hydroxides, isoelectric at or above pH 7.0, show only a negligible cation adsorption at this pH.

If the pH of the barium acetate is adjusted to the isoelectric pH of the colloid no trace of barium exchange is obtained, so that for these hydroxides at least there is no cation exchange if the colloid is leached with a solution the pH

of which corresponds to the isoelectric pH. With soil colloids, however, a small degree of cationic exchange is always observed under similar conditions (1, V), an overlapping of both cationic and anionic adsorption taking place at the isoelectric pH, so that the common anions are adsorbed slightly at a pH above the isoelectric pH of the colloids, and the common cations to a small extent below this point, the extent to which the exchange of both anions and cations overlap at the isoelectric point being greater the more strongly adsorbed or the least dissociated the ions.

ANION ADSORPTION

While the cationic adsorption was studied under leaching conditions, so that the reaction is thrown in one direction by removal of the acetic acid formed, the study of anion adsorption was done under equilibrium conditions, and the oxalate ion in these preliminary experiments was found to be very suitable. Half-gram portions of the dried isoelectrically precipitated hydroxides were allowed to come to equilibrium over a 24-hour period with a 100-cc. solution containing 1.70 m.e. of oxalate. Variations in pH were obtained by altering the amounts of oxalic acid or ammonium oxalate used, both of the same concentration, so that the oxalate concentration was maintained constant. The pH values above the neutral point were obtained by the addition of ammonia. The results obtained with aluminum, titanium, ferric, and stannic hydroxides are shown in table 132, and are graphically represented in figure 38.

Within the pH range where all the four colloids remain insoluble and coagulated, the adsorption of oxalate is greatest by that hydroxide which has the highest isoelectric point, whereas the adsorption of barium increases in the reverse order. The adsorption of anions increases with a decrease in pH, whereas the adsorption of cations increases with increasing pH from the isoelectric pH.

Apart from the distinct correlation between the isoelectric pH and the adsorption of ions, the actual magnitude of the adsorption has in this connection no great significance, because of the considerable solubility effects that are introduced. Aluminum hydroxide at the lowest pH (4.5) adsorbs less oxalate than at the next pH, which must be due to the solubility of the compound formed on adsorption. Other factors also influence the degree of adsorption, such as aging and the degree of polymerization of the molecules that constitute the ionic micells.

Magnesium hydroxide, a strongly basic compound, fails to show a trace of adsorption at any pH, the oxalate ion apparently being too highly dissociated to displace the OH ion, which on the alkaline side suffers a suppressed dissociation.

The adsorption of the sulfate anion was determined with iron, aluminum, and magnesium hydroxides. Sodium sulfate and sulfuric acid, of the same con-

centration were used, variation in pH being introduced by varying the proportion of sodium sulfate and sulfuric acid. The results are shown in table 133.

Again magnesium hydroxide failed to show any anion adsorption, presumably because this ion is too highly dissociated and the compound too soluble. The aluminum and ferric hydroxides adsorb sulfate to a considerable extent, as was expected from previous work on the isoelectric precipitation of

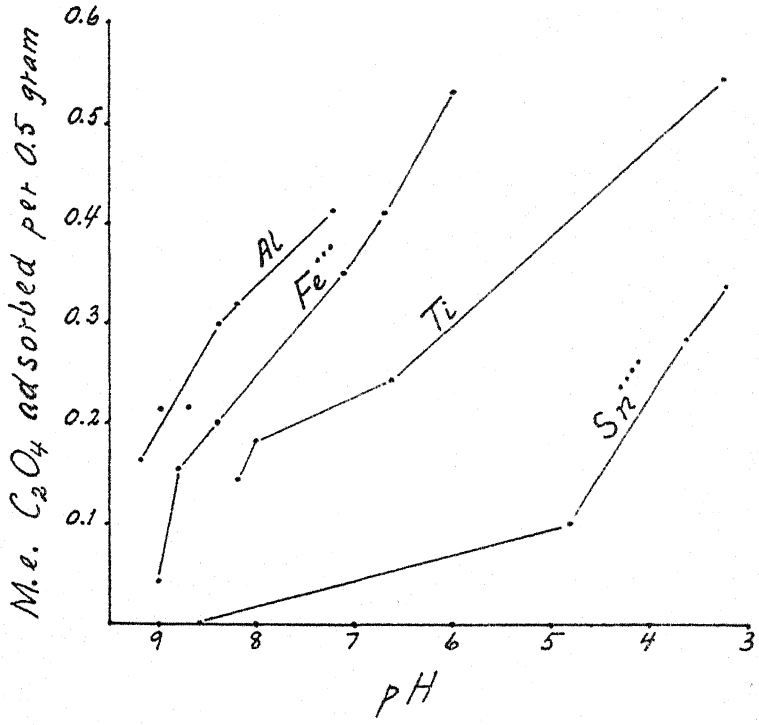


FIG. 38. THE ADSORPTION OF THE OXALATE ION BY ALUMINUM (8.1), FERRIC (7.1), TITANIUM (4.8), AND STANNIC (3.9) HYDROXIDES

(The figures in parenthesis give the isoelectric points of the hydroxides when precipitated from the chlorides.)

ferric and aluminum hydroxides prepared from the corresponding sulfates (1, III).

GENERAL DISCUSSION

On the basis of the theory of colloidal electrolytes largely developed by Michaelis (2), ampholytoids are to be regarded as colloids that dissociate both cations and anions and, conversely, adsorb both cations and anions depending on the conditions. An equilibrium exists between the ions and the undissociated micellae, just as exists between smaller ions in an ordinary electrolyte.

If the undissociated molecule is represented as HROH, it can dissociate in two ways, in the first place as an acid according to the equation:

$$K_a = \frac{(\mathrm{ROH})(\mathrm{H})}{\mathrm{HROH}} \qquad (A)$$

and then as a base according to the equation:

$$K_b = \frac{(\mathrm{HR})(\mathrm{OH})}{\mathrm{HROH}} \qquad (B)$$

where K_a and K_b are the ionization constants of the acidoid and basoid components. If the acid type of dissociation predominates, the isoelectric point will be at a low pH; conversely, if the basic ionization predominates the isoelectric point will be at a high pH. The isoelectric point corresponds to the neutral point when $K_a = K_b$.

If the values K_a and K_b could be determined for amphoteric colloids, the hydrogen-ion concentration I at the isoelectric point should theoretically be found from the expression

$$I = \sqrt{\frac{K_a}{K_b} \cdot K_w}$$

as in the case of soluble electrolytes. We cannot, however, by ordinary means determine the dissociation of a colloid, because the dissociated ions exist in the form of a swarm or atmosphere surrounding the particle whose concentration apparently increases toward the surface. The hydrion concentration we measure in a colloidal suspension represents the concentration in the solution, plus the effect of the dissociated ions in the micellar atmosphere. The latter effect increases with the concentration of the colloid and approaches a maximum in a stiff gel.

But apart from this difficulty, the isoelectric point varies with the nature of the anion adsorbed, being very often different for each compound. Although the amphoteric soluble electrolytes such as the amino acids have a well-defined isoelectric point which is independent of the nature of the salt used for determining it, the different compounds formed by replacing the hydroxyl ion in a colloid by another ion will often have a new isoslectric pH. In colloids it is not only the H and OH ions which are slightly dissociated, but all other ions dissociate to a limited extent. Dissociation can proceed only until a certain critical potential is established, and in a highly multivalent complex this requires a comparatively small number of ions (1, II). Dissociation beyond this point must result in an increased dispersion, and a complete dissociation will lead to an ultimate dispersion reaching the molecular stage, in which case the material ceases to be a colloid.

An amphoteric colloid whose $K_a > K_b$ must in the free condition have an acid reaction and be negatively charged, since the H ions are more dissociated

than the OH ions. To render the colloid isoelectric, acid must be added to suppress the dissociation of the acid group and increase that of the basic group. The complex will be *isoionic* when the dissociation of its cations and anions are equal but it might not thereby become isoelectric.

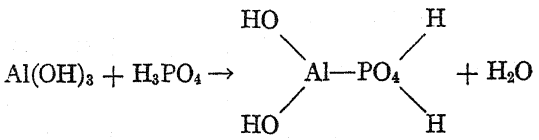
In the case of soluble ampholytes which form *completely dissociated* salts the quantity of acid required is always very small, and theoretically independent of its nature. But in the case of colloids which undergo a *limited dissociation* the quantity may be large and varies greatly depending upon the degree of dissociation of the compound formed. Thus if the OH ions are displaced by an ion which dissociates to a lesser degree than the former there can be no gain but rather a diminution in the positive charge, and the complex cannot become isoelectric. It might be assumed that, if the pH be lowered sufficiently, the colloid, in spite of this, will become isoelectric and finally electropositive as a result of a suppression of the hydrion dissociation. This is not necessarily the case, however, for all inert colloids charge themselves electronegatively in water, and this residual negative charge must be balanced by a certain degree of anionic dissociation before the colloid can be isoelectric. If, therefore, the anions be very slightly dissociated, the colloid, although it be amphoteric and in its isoionic condition, may not become isoelectric but remain electronegative, or it may show an isoelectric point considerably below its isoionic point. This might account for the fact that the fairly strong bases of divalent Cu and Mn were found isoelectric at pH values as low as 7.6 and 7.05 and that Bi stays electronegative in spite of its strong basic and faintly acidic nature.

The low dissociation of Cl ions from bismuth oxychloride probably accounts for the fact that this compound remained electronegative down to pH 2.8, whereas antimony trioxide was found to be isoelectric at pH 5.6. From this, one should have expected bismuth to have a still higher isoelectric point, since the element is the more basic of the two (3).

That the isoelectric point of "hydroxides" varies with the nature of the anion in combination has previously (1, III) been shown in the case of aluminum and iron. Aluminum hydrous oxide precipitated from the chloride by the addition of NaOH was isoelectric at pH 8.1, and had a composition expressed by the formula $(Al_2O_3)_{4\cdot16} \cdot Al_2O_2Cl_2$, whereas the sulfate yielded a compound isoelectric at pH 7.6 and with the composition $(Al_2O_3)_{12\cdot5} \cdot Al_2O_2SO_4$. The difference in the isoelectric points as well as in composition must be ascribed to a difference in dissociation, the SO_4 ions obviously being less dissociated and displacing a greater number of OH ions than the Cl ions. The phosphate ion caused a still greater deflection of the isoelectric point toward the acid side, a compound of the composition $Al_2O_3 \cdot (P_2O_5)_{0.86}$ being isoelectric at pH 4.9. It is not the hydroxide which is isoelectric at different pH values but a complex whose composition varies constantly with a change in reaction and the ionic environment in general. This change in composition is the most potent factor in causing a change in the electrokinetic behavior and chemical properties. It

not only alters the dissociation of the acid and basic groups but very often adds new groups or inactivates those already present. In this way the acid group may be strengthened and the basic group weakened or vice versa.

Thus if the OH ions be displaced by a polybasic acid such as H_3PO_4 a new acid group may be introduced whereas the basic group has been weakened according to the following equation:



If the union between Al and PO_4 results in a practically non-dissociated compound, it is clear that the dissociation of the basic group has been permanently reduced. In addition there has been introduced an acid residue which adds greatly to the acid dissociation of the colloid. This explains the lowering of the isoelectric point and the increase in the cation exchange capacity observed in the case of phosphated, silicated, and humated sesquioxides (1, V).

The precipitation of the amphoteric hydroxides may be illustrated as follows:

$$Al^{+++} \rightarrow AlOH^{++} \rightarrow Al(OH)_2^{+} \text{ etc.}$$

With decreasing dissociation, and decreasing colloidal dispersion, a floc with the following formula may be formed:

$$[Al(OH)_3]_x \cdot [Al(OH)_2]_z^{+} + zCl^{-}$$

In this scheme the value of x is assumed to increase in the direction of the isoelectric point. It is obvious that we have every transition in dispersion and charge all depending upon the degree of dissociation. When the charge of a particle falls below a certain critical value an association of two or more particles results until the ionic density and charge is again such as to maintain a stable condition. There is no discontinuity between the "crystalloid" and colloid conditions of matter; the one merges imperceptibly into the other.

The extension of the zone of flocculation and therefore the degree of dispersion depend upon the dissociation of the diffusible ions in combination. Ca and SO_4 ions in combination with most ampholytoids are less dissociated than Na and Cl ions. The former give, therefore, a wider zone of flocculation.

Since the ampholytoids are weak acids and bases, their salts all undergo more or less extensive hydrolysis, and, since the diffusible ions can be removed by leaching, dialysis, and electrodialysis, these processes all lead to the unsaturated condition, the pH thereby changing in the direction of the isoelectric point. An amphoteric colloid is most easily "purified" at the isoelectric point. This is taken advantage of in analytical chemistry. Thus stannic acid is precipitated for gravimetric estimation by precipitation with ammonia, to the methyl orange end point (pH 3.1 – 4.4), whereas the isoelectric pH of the

compound is about pH 3.9. Ferric and aluminum hydroxides isoelectric when precipitated from their chlorides at pH 7.1 and 8.1 respectively are precipitated with ammonia at about the neutral point. At the isoelectric point (or perhaps more strictly at the isoionic point) the dissociation of an amphoteric compound is at a minimum and the cationic and anionic dissociations are equal. An amphoteric colloid is therefore least soluble, least dispersable, and most stable at the isoelectric (or isoionic) point. These are the fundamental principles which form the basis of the theory of isoelectric weathering (1, IX).

SUMMARY

This paper deals with the isoelectric point and ionic exchange of a number of hydrous oxides.

A general relationship is observed between the position of the isoelectric point and the acidic or basic properties of the elements. Their electrokinetic behavior, however, is not always indicated by their position in the periodic table, apparently because of differences in dissociation of the various compounds and of the fact that the isoelectric point does not coincide with the isoionic point.

The hydrous oxides isoelectric below pH 7.0 adsorb and exchange cations at this pH, a capacity which increases as the isoelectric pH decreases. The adsorption of anions increases with diminishing pH, in the reverse order to cationic adsorption.

REFERENCES

(1) MATTSON, SANTE 1929–1932 The laws of soil colloidal behavior: II. Cataphoresis, flocculation, and dispersion. *Soil Sci.* 28: 373–409 (1929); III. Isoelectric precipitates. *Soil Sci.* 30: 459–495 (1930); IV. Isoelectric precipitates. *Soil Sci.* 31: 57–77 (1931); V. Ion adsorption and exchange. *Soil Sci.* 31: 311–331 (1931); IX. Amphoteric reactions and isoelectric weathering. *Soil Sci.* 34: 209–240 (1932).

(2) MICHAELIS, L. 1922 Die Wasserstoffionenkonzentration, v. 1. Berlin.

(3) PARBERRY, N. H., AND MATTSON, SANTE 1932 Electrokinetics and base exchange capacity of some inorganic colloids. *Soil Sci.* 33: 75–94.

(4) POWIS, F. 1915 *Ztschr. Phys. Chem.* 45: 307.



LAWS OF SOIL COLLOIDAL BEHAVIOR: III. COLLOIDAL PHOSPHATES[1]

A. J. PUGH[2]

New Jersey Agricultural Experiment Station

Received for publication October 7, 1933

Previous investigations by Mattson have shown that the colloidal materials of soil and other colloids divide themselves electrokinetically into positive and negative colloids, depending to a considerable extent on the pH of the medium, the composition of the colloid, and the ratio of $\frac{\text{acidoid}}{\text{basoid}}$.

Positive and negative colloids mutually flocculate each other, forming new compounds, the ionic exchange capacity of which vary with the composition and the position of the isoelectric point with respect to the pH. Different ions enter the micelle and form part of the molecule, and with this difference in composition there will be a difference in the degree of dispersion and solubility at any pH. This variation in physical properties with composition gives rise to the development of horizons in soils. Hydrolysis of the soil and dispersion of the particles take place in one layer, followed by migration of the dispersed particles through the soil to another layer where, because of differences in pH, the particles again combine and flocculate.

In several publications by Mattson (13) the isoelectric precipitations of a large number of compounds were recorded. In the present work this study has been extended to include a fairly complete range of phosphate compounds that may arise in the soil by hydrolysis or by addition in the form of fertilizers.

EXPERIMENTAL

Accurately measured portions of the two solutions A and B to be mixed were placed in separate tubes, and sufficient water was added to make the total volume 50 cc. The variation in pH was introduced by adding HCl or NaOH, the HCl being added to the salt solutions and the NaOH to the phosphate solutions.

[1] Editor's note: Papers I and II of Pugh's series "Laws of Soil Colloidal Behavior" were erroneously included in Mattson's series "Laws of Soil Colloidal Behavior" as papers XIV and XV (SOIL SCIENCE 37: 403; 38: 161).

Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

[2] The author desires to thank Dr. Sante Mattson for suggesting this problem and for his advice during the progress of the work. Thanks are also due to the British Ministry of Agriculture for a research scholarship during the tenure of which this work was carried out.

The flocculation after the solutions were mixed and after they were allowed to stand overnight are recorded in the tables. The latter is represented by the usual notation of x signifying slight, xx about half complete, xxx nearly complete, and xxxx complete flocculation. The phosphate in the supernatant liquid was determined either by the Fiske and Subbarow (8) or by the Deniges (7) method, and the pH by the quinhydrone electrode or colorimetrically. Cataphoresis measurements were made on the remaining suspensions.

STRUCTURE OF PHOSPHATES

Phosphatic compounds are frequently represented as double salts or molecular compounds with a formula such as $Ca_3P_2O_8 \cdot Ca(OH)_2$. Although justification for such a formulation could hardly be obtained, the use of such formulas became general because at the time there was no other adequate theory which could displace the older conception, until Werner introduced his theory of co-ordination. With the development of the theories of atomic structure and of valency by Bohr (2), Bury (4), Lewis (10), and Sidgwick (19), a reasonable explanation for the existence of the co-ordination compounds of Werner was obtained by Lewis. These theories (16) have been applied in a previous paper to interpret the phenomena of aging in colloids with aluminum hydroxide and silicate. The same theory can be applied to phosphates and is rendered necessary in order to explain the nature of the reaction that takes place in a colloidal micelle with a differentiation in the hydrogen-ion concentration of the liquid phase.

The recent advances in the development and interpretation of base exchange reactions were made possible because of the recognition that the hydrogen ion at the surface of the colloidal anion takes its part with other cations in exchange reactions. Although the position of the hydrogen ion is thus moderately well defined, the part played by the hydroxyl ion is uncertain and has not been the subject of extensive investigation, because in ion exchange reactions, as in most surface reactions, peculiarly little attention has been paid to the composition of the colloidal anion. It is in the latter respect that the hydroxyl ion becomes the dominating ion, and it is with that purpose in view that this preliminary work on phosphates has been done.

The influence of pH on the adsorption of ions by hydroxides (16) showed that at a pH below the isoelectric pH of the colloid, there was exchange alkalinity, that is, a hydroxyl ion entered the solution as the anion, whether sulfate or oxalate, entered the colloid. Such an adsorption is obviously a pronounced exchange reaction, of the same nature as base exchange, and it proceeded without any obvious alteration in the physical properties of the colloidal micelle over a considerable pH range. In the preparation of these phosphate compounds, it was also observed that as the hydroxyl ion exceeds a certain concentration, the PO_4 ion is being replaced by the hydroxyl group, and the ratio of $\frac{P_2O_5}{R_xO_y}$ is diminished as the pH is increased, but the solubility and physical

properties of the micelle are not altered by the change. Thus with stannic phosphate at pH 2.2, the molecular ratio of $\frac{SnO_2}{P_2O_5}$ is 6.2, but at pH 3.75 it is 12.40.

Representing phosphates as molecular compounds does not permit of an explanation of such an exchange, but an analogous phenomenon takes place in the Werner compounds where a whole group such as NH_3 can be replaced by a simple atom like chlorine. Nitrogen, atomic structure (2) (5),[3] combines with three hydrogen atoms each with a lone valence electron, and by sharing of electrons it reaches the stable number of neon (2) (8), and hydrogen the stable number of helium (2), thus

$$\begin{array}{c} H \\ \cdot\cdot \\ H:\underset{\cdot\cdot}{N}:H \end{array}$$

This leaves the nitrogen of the ammonia with a lone pair with which it can combine with another atom thus forming a co-valent bond. A characteristic change of electrovalency accompanies substitution in the co-ordination zone. Thus,

$$\left[\begin{matrix} Pt(NH_3)_2 \\ Cl_2 \end{matrix}\right]$$

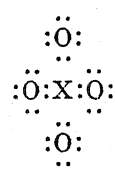
If a neutral chlorine atom is removed, it will take with it one of the pair of electrons which it previously shared with the platinum, and the other is left behind. If now the ammonia molecule takes its place, this provides the two electrons necessary for the attachment, so that platinum has gained one electron by the exchange. It had already in the original compound the requisite number of electrons for stability, but it has now one too many. It will lose this to the displaced chlorine atom forming an electrovalency, and a salt $\left[\frac{Pt(NH_3)_3}{Cl}\right]Cl$ is formed.

In the complexity of their composition, colloids show many similarities in properties to Werner compounds, but have as well other properties due to the presence of a hydroxyl group, and in particular of the hydrogen ion that arises during dissociation, for the strong adsorption of this ion must be attributed to the ease with which it can form a co-valency with a lone pair of electrons, and its high mobility due to its small volume.

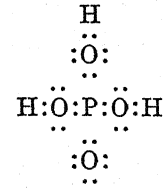
Phosphorus with atomic number (15) and electronic structure (2) (8) (5) acts both as a trivalent and as a quinquevalent element. It can combine with three hydrogen atoms, and, by sharing the valency electrons, reach the stable number of argon (18) with the formation of PH_3. Arising out of the electronic conception of valency, a very interesting formulation of phosphoric acid H_3PO_4

[3] The number in parenthesis immediately following the name of the element refers to its atomic number or electronic arrangement.

was suggested by Lewis. A co-ordinate co-valency arises out of one atom contributing both of the electrons that form a single link. With the oxy-acids of the type H_nXO_4 the eight shared electrons in the ion

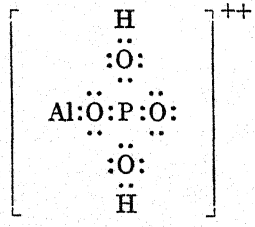


are all needed to make up the valency electrons of the oxygen (2) (6) from six to eight and must be derived from the central atom or outside. If X is phosphorus with five valence electrons to start with, it will require three more, which it obtains from three hydrogen atoms with the formation of H_3PO_4.



The formulation of phosphoric acid in this way gives to phosphorus a maximum co-valency of four, a group of eight shared electrons. There is no doubt that with a large number of compounds the maximum co-valency is four, but with PCl_5 its maximum co-valency is five, a group of ten shared electrons.

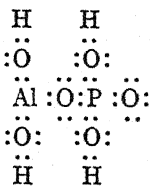
The formation of aluminum phosphate from aluminum chloride and phosphoric acid can be represented as follows. Aluminum, atomic number (13) and electronic structure (2) (8) (3), gives an electron to each chlorine atom (2) (8) (7). In solution these dissociate, and the chlorine takes away the bonding pair of electrons. The phosphoric acid combines through the lone pair of an oxygen atom forming the ion



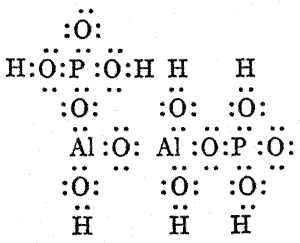
This saturates one valence of the aluminum, whereas a co-valency of three could be satisfied by a greater dissociation of the phosphoric acid, with three oxygen atoms of the PO_4 ion combining with the aluminum through their lone pairs. The hydroxyl, phosphoric acid, silica, and also chlorine ions can enter simultaneously, depending on the maximum co-valency formation that the

aluminum is capable of achieving, and the fact that the proportion in which each of them would contribute to the saturation of the central atoms would be determined by the law of mass action and the stability of each co-valency. In the present work this has not been investigated because only the pH and not the concentration of hydroxyl ions has been determined.

The formation of a colloidal micelle with phosphates can take place in the same way as with aluminum hydroxide and silicate, by continuous polymerization of the molecules. If we represent a phosphate in the original molecular stage as



only the first dissociation of phosphoric acid into H^+ and $H_2PO_4^{-}$ is assumed. If now the hydrogen wanders from the hydroxyl group of this molecule, then the whole molecule can combine, through the lone pair of the oxygen, with another molecule, by the oxygen from which the hydrion has left giving its lone pair of electrons toward the saturation of the aluminum. This, as with hydroxides and silicates (16), leads to indefinite polymerization, the valency of the aluminum increasing from three to four, and the internal central atom becomes saturated, but the whole micelle or giant molecule will be capable of indefinite polymerization because of the unsaturation of the surface aluminum atom. The molecule would have the following hypothetical structure:



With complete dissociation of the phosphoric acid, three oxygen atoms of the trivalent PO_4 ion would give their lone pair of electrons toward the saturation of the central atom.

Just as the substitution of chlorine for ammonia is rendered possible in Werner compounds, by the fact that the ammonia has a lone pair of electrons and can replace the chlorine bond unit by unit, so in phosphates the hydroxyl ion $:\ddot{O}:H$, with the "lone pair" of the oxygen, can displace the bond formed by the oxygen of the phosphoric acid. As long as only a small percentage of the

phosphoric acid is thus replaced, it is probable that too great a variation in the physical properties of the micelle is not produced by the substitution, which could thus proceed within certain limits of pH. Too high a concentration of hydroxyl ions would, however, introduce hydrolysis at the central bonds, with the possible secondary effects of dispersion and solubility. The number of hydroxyl ions required to displace the surface phosphoric acid will depend on the number of oxygen atoms that combine with the central atom. If all the bonds are utilized, then three hydroxyl groups would be required to displace a PO_4 group.

Mattson (13) has demonstrated that phosphates have a lower isoelectric pH than the corresponding hydroxides of the metal. For the synthesis of the ionic micelle a certain concentration of anions, whether hydroxyl ion or phosphoric acid ions, is necessary. If the hydroxyl ion is the only anion that contributes towards the saturation of the central atom, then a comparatively high pH will be required for the formation of the micelle. If other ions are added that can contribute to the saturation of the central atom, then a micelle will be formed at a lower pH, but a certain concentration of hydroxyl ions is necessary in all cases in order to prevent acid hydrolysis.

The linkages formed between the phosphoric acid, hydroxyl ions, and the central atom, where the bonding pair of electrons come from one and the same atom, are thus in all cases co-ordinate co-valency bonds. From the viewpoint of colloid chemistry the properties of compounds with co-ordinate co-valent linkages that are of importance are: (*a*) They have an open structure and occupy a large volume as compared with simple crystals, e.g. sodium chloride; (*b*) Compared with compounds containing electrovalent bonds they exhibit considerable stability; (*c*) The forces are directed forces that proceed from atom to atom, and form an integral part of the constitution of each molecule, whereas in those compounds with electrovalencies the forces are from ion to ion, and a stable chemical bond is not achieved, for unlike co-valent compounds they are ionized even in the solid state.

A question that remains to be answered is whether on suspension in water the non-dissociated portion is wholly held together by electrovalent links, or whether it forms ions and partly dissociated co-valent molecules. The whole phenomenon of ion exchange as investigated by Mattson (13) and for hydroxides by the author, point to the latter conclusion. The phenomenon of ion exchange is due to the dissociation of hydrions or hydroxyl ions from the surface of the amphoteric colloids, which leaves the main body of the micelle untouched and still in the co-valent form. At the isoelectric point the dissociation is at a minimum, but its position with respect to the pH is a function of the specific properties of the colloid, that is, its strength as an acid or base. In the unsaturated condition the surface of the micelle consists of hydroxyl groups, and the pH of the salt solution used to determine the ion exchange alters both the degree and the nature of the dissociation due to mass action. In terms of atomic structure the ratio of the co-valent to the electrovalent form

is a maximum at the isoelectric point, that is, the dissociation is least, and since ion exchange can take place only as a secondary reaction to dissociation, the ion exchange is a minimum when the colloid is treated with a solution the pH of which corresponds to the isoelectric pH.

The dissociation of hydrions or hydroxyl ions from the surface of a phosphatic micelle will, as in the case of a soil, give ion exchange reactions, subject to the limitations imposed by the position of the isoelectric point with respect to the pH. The fact that Mattson (13) found that iron and aluminum phosphates have considerable base exchange capacity at pH 7, proves this to be true. The formulation of phosphates in this manner, although as yet indefinite, is

TABLE 1

The $SnCl_4$ + Na_2HPO_4 system

A. 20 cc. of $SnCl_4$ solution (10 m.e. SnO_2 per liter)
B. 20 cc. of Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.492	Rapid	xxxx	— slow	2.10	1.56	0.86
.....	0.246	Rapid	xxxx	— slow	2.30	1.58	0.84
0.027		Rapid	xxxx	— slow	2.83	1.67	0.75
0.123		Rapid	xxxx	— slow	3.32	1.74	0.68
0.148		Rapid	xxxx	— slow	4.11	1.85	0.57
0.197		Clear	Clear		7.00		

200 cc. $SnCl_4$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	SnO_2 ADDED	SnO_2 IN SOLUTION	SnO_2 IN PRECIPITATE	P_2O_5 IN SOLUTION	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{SnO_2}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
2.19	75.6	Trace	75.6	15.50	8.70	6.19
2.40	75.6	Trace	75.6	16.87	7.33	9.73
3.75	75.6	Trace	75.6	18.01	6.19	12.40

more reasonable than an assumption of the existence of a molecular compound, but because of the lack of precise information no hypothetical formula is attempted, but the composition of each is discussed in its bearing on soil problems.

Stannic and titanic phosphates

The quantity of phosphate, the pH of precipitation, and the cataphoretic mobilities of stannic and titanic phosphate precipitates are shown in tables 1 and 2. Stannic phosphate has no isoelectric point at any finite pH, the acid-dissociation being much too strong, whereas titanium has an isoelectric point at a low pH. The quantity of phosphate adsorbed is very small but definite.

In acid solutions both are very stable, but are dispersed at pH 6.0. Tin does not exist in the colloid fraction of the soil, but titanium does in small quantities of about 1 per cent TiO_2, as found in the colloid fractions investigated by Robinson and Holmes (17), and by Byers, Anderson, and Brown (3, 5). Upon acid extraction of a soil, a part of the phosphate will be retained in insoluble form by combination with titanium. Ward (20), found it necessary, with Hawaiian soils, to fuse with Na_2CO_3 the residue after acid extraction in order to obtain all the phosphate, because of the unusually high percentage of titanium that these soils contain, with the precipitation of phosphate in strongly acid solutions.

TABLE 2

The $TiCl_4$ + Na_2HPO_4 system

A. 20 cc. of $TiCl_4$ solution (10 m.e. TiO_2 per liter)
B. 20 cc. of Na_2HPO_4 solution (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.197	Rapid	xxxx		2.40	1.61	0.81
.....		Rapid	xxxx	+ slow	2.80	1.61	0.81
0.098		Rapid	xxxx	−1.51	3.35	1.72	0.70
0.123		Rapid	xxxx	−2.02	3.71	1.72	0.70
0.137		Rapid	xxxx	−3.03	4.82	2.08	0.34
0.148		Turbid	Turbid		6.28		

200 cc. $TiCl_4$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	TiO_2 ADDED	TiO_2 IN SOLUTION	TiO_2 IN PRECIPITATE	P_2O_5 IN SOLUTION	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{TiO_2}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
2.37	40.0	Trace	40.0	19.04	5.16	13.6
2.92	40.0	Trace	40.0	19.04	5.16	13.6
3.80	40.0	Trace	40.0	20.20	4.00	17.7

Ferric and aluminum phosphates

Ferric and aluminum phosphates have previously been investigated by both Mattson (13) and Gaarder (9). The results obtained with these phosphates at three different concentrations of phosphate, keeping the bases constant, are shown in tables 3 to 7.

The zone of precipitation of ferric and aluminum phosphates, with respect to the pH, extends much more to the acid side than with the hydroxides alone. The phosphates also have a lower isoelectric pH than the corresponding hydroxides.

With increasing pH, the amount of phosphate in the precipitates diminishes,

TABLE 3

The $FeCl_3$ + Na_2HPO_4 system

A. 20 cc. of $FeCl_3$ (10 m.e. Fe_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		Immediate	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.123		Clear	Clear		4.23		
0.128		Rapid	xxxx	+ slow	4.78	0.06	2.16
0.133		Rapid	xxxx	−1.51	5.18	1.00	1.42
0.138		Rapid	xxxx	−1.89	5.85	1.00	1.42
0.143		Clear	Clear		6.31		

200 cc. $FeCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Fe_2O_3 ADDED	Fe_2O_3 IN LIQUID	Fe_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Fe_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
5.6	53.2	Trace	53.2	Trace	24.20	1.95
6.2	53.2	Trace	53.2	0.92	23.28	2.03
6.4	53.2	Trace	53.2	1.85	22.35	2.11

TABLE 4

The $FeCl_3$ + Na_2HPO_4 system

A. 20 cc. of $FeCl_3$ (10 m.e. Fe_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		Immediate	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.148	Turbid	xxxx	+ rapid	2.85	4.90	4.78
.....	0.074	Opal	xxxx	+2.02	3.33	5.26	4.42
.....	0.010	Rapid	xxxx	+0.60	3.79	5.26	4.42
.....		Opal	xxxx	−1.01	3.80	5.26	4.42
0.020		Clear	x		4.90		

200 cc. $FeCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Fe_2O_3 ADDED	Fe_2O_3 IN LIQUID	Fe_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Fe_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
2.6	53.2	Trace	53.2	46.75	50.05	2.41
3.6	53.2	Trace	53.2	50.00	46.80	2.58
4.6	53.2	Trace	53.2	51.29	45.51	2.65

TABLE 5

The $AlCl_3$ + Na_2HPO_4 system

A. 20 cc. of $AlCl_3$ (10 m.e. Al_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.118		Clear	Clear				
0.129		Opal	Opal		5.58		
0.132		Rapid	xxxx	±0.00	6.10	0.083	2.14
0.138		Rapid	xxxx	− slow	6.51	0.620	1.80
0.143		Clear	xxxx	− slow	6.65	0.670	1.75
0.148		Clear	x	− rapid	7.00		

200 cc. $AlCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Al_2O_3 ADDED	Al_2O_3 IN LIQUID	Al_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Al_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.1	34.10	4.2	29.90	0.53	23.67	1.75
6.6	34.10	2.8	31.30	2.45	21.75	1.99

TABLE 6

The $AlCl_3$ + Na_2HPO_4 system

A. 20 cc. of $AlCl_3$ (10 m.e. Al_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (4.84 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.069		Clear	Clear		4.75		
0.079		Rapid	xxxx	+2.75	5.01	0.53	4.31
0.089		Rapid	xxxx	+1.51	5.33	1.23	3.61
0.099		Rapid	xxxx	±0.00	6.11	1.45	3.39
0.109		Slow	xxxx	− slow	6.38	2.85	1.99
0.119		Clear	Clear		7.50		

200 cc. $AlCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Al_2O_3 ADDED	Al_2O_3 IN LIQUID	Al_2O_3 IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{Al_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
5.0	34.10	1.4	32.7	11.57	36.83	1.23
6.4	34.10	5.2	28.9	17.24	31.16	1.29

the hydroxyl ion replacing the PO_4. Both acid and alkaline hydrolysis occurs, and there is an optimum pH at which these compounds can be precipitated. This is about the isoelectric pH, but flocculation extends to both sides. The quantity of phosphate adsorbed in the precipitate need not be a maximum at the isoelectric pH, for both OH and PO_4 ions enter into the structure of the ionic micelle, and which predominates at the isoelectric point is not known. Under natural conditions, the soil colloid by hydrolysis goes through a structural re-arrangement so that its composition will correspond to its isoelectric pH, as has been found to be the case by Mattson (13).

TABLE 7

The $AlCl_3$ + Na_2HPO_4 system

A. 20 cc. of $AlCl_3$ (10 m.e. Al_2O_3 per liter)
B. 20 cc. of Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	Flocculation		μ/sec. 1 volt/cm.	pH	P_2O_5 in supernatant liquid	P_2O_5 in precipitate
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....	0.010	Clear	Clear		4.45		
0.005	0.000	Rapid	xxxx	+0.81	5.01	5.51	4.17
0.010	0.000	Rapid	xxxx	+0.76	5.47	5.66	4.02
0.015	0.000	Rapid	xxxx	−0.76	5.53	5.66	4.02
0.020		Rapid	xxxx	−0.84	5.93	5.66	4.02
0.030		Slow	xxxx	−1.51	6.41	5.66	4.02
0.040		Clear	Clear		7.00		

200 cc. $AlCl_3$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	Al_2O_3 added	Al_2O_3 in liquid	Al_2O_3 in precipitate	P_2O_5 in liquid	P_2O_5 in precipitate	Mol. ratio $\frac{Al_2O_3}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
4.9	34.10	Trace	34.10	52.21	44.59	1.00
5.2	34.10	Trace	34.10	54.05	42.75	1.11
6.4	34.10	Trace	34.10	57.80	39.00	1.22

Calcium and magnesium phosphates

An apparent difficulty arises with calcium and magnesium phosphates if they are represented as was the aluminum phosphate, on the basis of atomic structure and the modern conception of valency. Magnesium, atomic number (12) and electronic structure (2) (8) (2), combines with chlorine to give a highly dissociated compound. Calcium, atomic number (20) and electronic structure (2) (8) (8) (2), does the same. That this type of structure is highly dissociated was taken as evidence, in the work on aging of colloids, that in base exchange, at the surface of the particle, the magnesium and calcium could be held only by electrostatic attraction, the bond (2) (8) (2) not being a true bond.

A different viewpoint can, however, be obtained if the calcium and magne-

sium be regarded as the central atom. In a soil particle swathed with a water medium, since the solution contains very little silica, phosphate, or any of the polyvalent anions, the only anion is the giant polyvalent anion of the soil itself, the surface exchangeable bases being added after the polymerization of the colloidal micelle was complete. Both calcium and magnesium form the compounds $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ in the solid form, which on Werner's theory would be represented somewhat as follows:

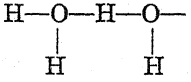
$$\begin{bmatrix} H_2O & & H_2O \\ H_2O & Ca & H_2O \\ H_2O & & H_2O \end{bmatrix} Cl_2$$

Magnesium has a much greater tendency to take on the co-valent form than calcium, which it does in the Grignard reagent with ether:

$$(C_2H_5)_2O \rightarrow Mg(OH)(I) \leftarrow O(C_2H_5)_2$$

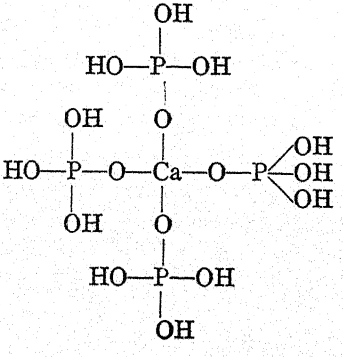
where the magnesium has a group of eight shared electrons, a co-valency of four, the ether being the "donor molecule," that is, the one that gives the extra electrons to the magnesium.

With both $CaCl_2 \cdot 6H_2O$ and $MgCl_2 \cdot 6H_2O$ an analogous situation arises. Water has the remarkable property of associating, that is, one simple molecule combining with another simple molecule to form a chain as follows:



This is a molecule in which the end oxygen has a lone pair of electrons or a single bond which is not utilized in combination. It has also a di-valent hydrogen which renders it unstable so that it can break easily into simple H_2O units.

This is the possible cause of hydration of ions on chemical grounds. In the formation of calcium and magnesium phosphates an analogous reaction may occur, the central atom, as with aluminum, taking on a very high co-valency of 4 or 6, forming as before a highly polymerized molecule, and ultimately a micelle, which could be represented simply as:



The surface hydrogen, that of the hydroxyl group, is the one that dissociates and is replaced by calcium or magnesium if present in excess. A combination like this, however, is probably stable only in the presence of considerable excess of anions, either hydroxyl or phosphate, and the phosphates of both calcium and magnesium are precipitated at a high pH.

As with the phosphates of the other elements, the phosphates of both calcium and magnesium show a variation in composition with pH and with increased concentration of phosphate, as shown in tables 8 to 13. Magnesium phosphate

TABLE 8

The $CaCl_2$ + Na_2HPO_4 system

A. 20 cc. $CaCl_2$ (10 m.e. CaO per liter)
B. 20 cc. Na_2HPO_4 (2.42 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.010		Clear	xxxx	0.00	6.8	1.95	0.47
0.028		Clear	xxxx	− slow	7.2	0.53	1.89
0.049		Clear	xxxx		8.2	0.10	2.32
0.059		Slow	xxxx	− slow	9.0	0.06	2.36
0.069		Rapid	xxxx		10.0	0.03	2.39
0.197		Rapid	xxxx		11.0	0.03	2.39
0.492		Rapid	xxxx		>12.0	0.03	2.39

200 cc. $CaCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	CaO ADDED	CaO IN LIQUID	CaO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{CaO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.8	56.0	42.5	13.5	13.6	10.59	3.20
9.0	56.0	35.1	20.9	0.1	24.1	2.20
12.0	56.0	23.6	32.4	Trace	24.2	3.40

is stable only around pH 10, and is very susceptible to both alkaline and acid hydrolysis, whereas calcium phosphate is more stable on the alkaline side but goes into solution at pH 6. Bassett (1), on the basis of some results obtained with calcium phosphate, suggested that in faintly alkaline solutions, the compound would have the structure $(Ca_3P_2O_8)_3\ Ca(OH)_2$, and Russell (18) suggests that calcium phosphate added to the soil would tend to be converted into this substance. The formula itself has no meaning, and since there is a large group of soils, the podzols, which have a pH considerably below that at which calcium phosphate can be formed, the formation of calcium phosphate is doubtful in most of them, the reversion taking place by combining with iron and aluminum.

TABLE 9

The $CaCl_2$ + Na_2HPO_4 system

A. 20 cc. $CaCl_2$ (10 m.e. CaO per liter)
B. 20 cc. Na_2HPO_4 (4.84 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....		Clear	Clear		6.0		
0.010		Clear	xxxx	±0.00	6.6	2.90	1.94
0.020		Slow	xxxx	±0.00	6.8	2.29	2.55
0.040		Rapid	xxxx	− slow	7.1	1.64	3.20
0.098		Rapid	xxxx		10.2	0.75	4.19
0.246		Rapid	xxxx		>12.0	0.75	4.19
0.492		Rapid	xxxx		>12.0	Very low	4.84

200 cc. $CaCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	CaO ADDED	CaO IN LIQUID	CaO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{CaO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.6	56.0	37.30	18.7	28.3	20.1	2.37
7.6	56.0	14.20	41.8	10.8	37.6	2.82
12.0	56.0	3.78	52.2	Trace	48.4	2.75

TABLE 10

The $CaCl_2$ + Na_2HPO_4 system

A. 20 cc. $CaCl_2$ (10 m.e. per liter)
B. 20 cc. Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.) } Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
.....		Clear	xxxx	−0.7	6.8	5.71	3.97
0.010		Clear	xxxx	−0.7	6.8	5.55	4.13
0.020		Slow	xxxx	−1.0	7.0	5.29	4.39
0.049		Rapid	xxxx	−1.51	7.8	5.19	4.49
0.069		Rapid	xxxx		8.8	5.19	4.49
0.089		Rapid	xxxx		10.2	5.19	4.49
0.246		Rapid	xxxx		11.2	5.19	4.49
0.492		Rapid	xxxx		12.0	5.19	4.49

200 cc. $CaCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	CaO ADDED	CaO IN LIQUID	CaO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{CaO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
6.8	56.0	17.0	39.0	57.8	39.0	2.53
7.6	56.0	5.2	50.8	48.0	48.8	2.65
12.0	56.0	3.3	52.7	48.0	48.8	2.75

TABLE 11

The $MgCl_2$ + Na_2HPO_4 system

A. 20 cc. of $MgCl_2$ solution (10 m.e. MgO per liter)
B. 20 cc. of Na_2HPO_4 solution (2.42 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.049		Clear	xxxx	−0.33	9.0	1.30	1.12
0.069		Opal	xxxx		10.0	0.38	2.04
0.079		Slow	xxxx	−0.45	10.0	0.42	2.00
0.148		Slow	xxxx		10.2	0.42	2.00
0.246		Slow	xxxx		10.3	0.80	1.62
0.492		Slow	xxxx	−1.51	>11.6	1.09	1.33

200 cc. $MgCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	MgO ADDED	MgO IN LIQUID	MgO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{MgO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
9.0	40.32	29.55	10.77	13.74	10.46	3.60
10.4	40.32	15.28	25.04	4.90	19.30	4.56
11.2	40.32	0.36	39.96	10.77	13.43	10.52

TABLE 12

The $MgCl_2$ + Na_2HPO_4 system

A. 20 cc. $MgCl_2$ (10 m.e. MgO per liter)
B. 20 cc. Na_2HPO_4 (4.84 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.059		Very slow	xxxx	−0.76	7.8	3.16	1.68
0.074		Slow	xxxx	−0.76	8.0	2.66	2.18
0.084		Slow	xxxx	−1.00	8.2	2.66	2.18
0.118		Slow	xxxx	−1.00	9.0	1.70	3.14
0.173		Slow	xxxx	−2.02	10.4	1.56	3.28
0.246		Slow	xxxx		10.6	1.56	3.28
0.492		Slow	xxxx		>12.0	2.54	2.30

200 cc. $MgCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	MgO ADDED	MgO IN LIQUID	MgO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{MgO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
8.2	40.32	27.52	12.80	33.80	14.60	3.09
10.0	40.32	13.47	26.85	21.79	26.61	3.56
11.2	40.32	Trace	40.32	29.94	18.46	7.61

TABLE 13

The $MgCl_2$ + Na_2HPO_4 system

A. 20 cc. $MgCl_2$ (10 m.e. MgO per liter)
B. 20 cc. Na_2HPO_4 (9.68 mgm. P_2O_5 in 20 cc.)
} Total volume 50 cc.

NaOH	HCl	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH	P_2O_5 IN SUPERNATANT LIQUID	P_2O_5 IN PRECIPITATE
		On mixing	Overnight				
m.e.	*m.e.*					*mgm.*	*mgm.*
0.025		Clear	Clear		7.74		
0.050		Slow	xxxx	−1.01	8.60	8.00	1.68
0.069		Slow	xxxx		9.20	7.31	2.37
0.089		Slow	xxxx	−1.2	10.10	7.00	2.68
0.108		Slow	xxxx	−1.5	10.20	6.37	3.31
0.173		Slow	xxxx	−1.6	10.20	6.25	3.43
0.246		Slow	xxxx		10.80	6.25	3.43
0.492		Slow	xxxx		>12.0	6.67	3.01

200 cc. $MgCl_2$ + 200 cc. Na_2HPO_4. Total volume 500 cc.

pH	MgO ADDED	MgO IN LIQUID	MgO IN PRECIPITATE	P_2O_5 IN LIQUID	P_2O_5 IN PRECIPITATE	MOL. RATIO $\frac{MgO}{P_2O_5}$
	mgm.	*mgm.*	*mgm.*	*mgm.*	*mgm.*	
8.4	40.32	24.91	15.41	75.94	20.86	2.59
10.2	40.32	10.07	30.25	63.69	33.11	3.23
11.0	40.32	Trace	40.32	68.59	28.21	5.41

ELECTROKINETIC POTENTIALS[4]

The interpretation of electrokinetic potentials presents considerable difficulties, but a great deal of confusion has arisen by limiting the outlook to compounds whose chemical structure is unknown, and by confining the viewpoint almost completely to the derivation of mathematical equations for calculating the charge. This has caused the neglect of most physicochemical changes which have a material influence on the nature and degree of potential acquired by soil colloids, such as the pH of the medium, exchange reactions that occur at the surface of colloidal micelles, and the great influence of solubility within a certain pH range. Michaelis (15) has emphasized the analogy between ordinary electrolytes and a very large class of colloids, and the work of McBain on soap solutions served further to demonstrate the relationship between the two.

While the Na-salts of the lower fatty acids in water form pure binary electrolytes, those of the higher fatty acids assume more and more colloidal properties. Their anion component no longer forms free ions, but rather micelles of fatty acids, with a surface dissociation. The existence of such a large polyvalent anion brings about electrostatic effects, with an extremely

[4] This discussion is drawn from the account as given by Michaelis, but has been added to, in order to bring soils, silicates, and phosphates into the same group.

strong electrostatic field in the neighborhood of the anion, whereby the cations while remaining free to move amongst themselves are distributed unevenly and are arranged in the form of a diffuse layer surrounding the anion. Under the influence of an applied potential the anions move in one direction and the cations in the other. Electrolytic conduction on this viewpoint is considered as a limiting case of cataphoresis where because of the high degree of dispersion of the dissolved substance the ions on the whole move independently of each other.

In certain aspects there are, however, important differences between dissolved electrolytes and colloidal electrolytes. With dissolved electrolytes, because of the small size of the ions, their mechanical and electrical mobilities are very high, and also in the special case of soap solutions McBain found that the electrical mobility of soap micelles approached those of smaller anions. Arrhenius in his well-known theory of electrolytic dissociation assumed the existence of ions, the dissociation increasing with dilution, but he further assumed that the electrostatic attraction and repulsion between the ions could be neglected in comparison with the mass action effect that they would display if they acted as molecules. His theory worked well with weak electrolytes but failed with strong electrolytes and was later substituted by the theory of Debye and Hückel (6), who, taking interionic forces into account and assuming a dissociation of 100 per cent, overcame the difficulties represented by the anomaly of strong electrolytes. Colloidal electrolytes, however, represent an extreme case, for here the electrostatic attraction between the micelles and the simpler ions of opposite sign is so great that it entirely dominates all other phenomena. The difficulties in the application of the theories for soluble electrolytes to colloidal electrolytes are, however, enormous. Although the similarity between a large number of colloids and electrolytes is quite obvious from the work of McBain (12), Michaelis (15), Loeb (11), and Mattson (13), there is as yet no definite quantitative expression.

Whereas the conductivity of soaps is high, the conductivities of soils are so very low as to give them the appearance of not being colloidal electrolytes, but actually they are, although very weak ones. Although Debye and Hückel's (6) theory of 100 per cent dissociation works well for strong electrolytes, the fact still remains that the original theory of Arrhenius of fractional dissociation is adequate for the interpretation of the dissociation of weak organic acids such as acetic acid, but not with their salts, which are strong electrolytes. The original assumption of Arrhenius of the existence of undissociated molecules with weak acids is undoubtedly correct, for the peculiar position of the hydrogen ion enables it to form a co-valency with the lone pair of electrons of the oxygen which is all that it requires to achieve stability

$$\left[\mathrm{X{:}\ddot{\underset{\cdot\cdot}{O}}{:}H}\right] \rightleftarrows \left[\mathrm{X{:}\ddot{\underset{\cdot\cdot}{O}}{:}}\right]\mathrm{H}$$

and a weak acid at ordinary dilutions exists largely in the co-valent form. Cations other than the hydrion require a valence group of eight electrons for stability and with a bond of the above type are electrovalent salts (10).

The silicates, the phosphates, and the soil have, from their most probable method of formation, a hydroxyl group at the surface, and the saturation capacity increases with the pH of the leaching solution. This, as has previously been stated, can be interpreted only on the basis that the dissociation of the hydrion is a function of the pH, and ion exchange is a secondary reaction. Because of the ease of formation of a co-valency between the oxygen and the hydrion their dissociation is weak and their conductivity values are low, as compared with soaps.

The question of the value of the determination of the isoelectric point and in particular of its correlation with pH and the saturation capacity naturally arises. Colloids are divided by Michaelis (15) into acidoids, basoids, and ampholytoids. Among the acidoids are the soaps investigated by McBain, and in the case of soil colloids those of extremely high silica content can function as pure acids. Ampholytoids consist of a large class of substances such as proteins, hydroxides, and nearly all soil colloids. With soluble ampholytoids the equation correlating the hydrogen-ion concentration with the strength of the acidity or alkalinity developed is correlated with the isoelectric point by the expression

$$I = \sqrt{\frac{Ka}{Kb} \cdot Kw}$$

where I = hydrogen-ion concentration at the isoelectric point, Ka Kb the dissociation constants for the acidoid and basoid components, Kw the dissociation constant for water. When the cationic and anionic dissociations are equal the isoelectric point is reached and the dissociation is at a minimum, but may vary enormously in degree from colloid to colloid.

It has previously been shown that the adsorption of anions from a salt solution by colloidal hydroxides (16) bears a distinct relationship to the exchange acidity or alkalinity developed, exchange alkalinity being developed if the colloid is treated with a salt solution, the pH of which was originally below the isoelectric pH of the colloid, and exchange acidity if the pH of the salt solution was originally above the isoelectric pH of the colloid, and the same reaction was found by Mattson and Hester to hold for a large number of compounds. During the formation of these phosphates by the substitution of chlorine by hydroxyl and phosphoric acid groups, sodium chloride is of course formed, and exchange of chlorine for hydroxyl and of sodium for the hydrogen ions can take place, depending on the pH of the salt solution and the isoelectric pH of the colloid. At a low pH when the colloid dissociates hydroxyl ions, the dissociation is suppressed by increasing the pH, and with a solution of high pH when the colloid dissociates hydrions the dissociation of these is suppressed by lowering the pH, and there is a consequent decrease in the electrokinetic potential.

Although the interpretation of electrokinetic potentials is thus complicated, the determination of the isoelectric point gives results of great practical value

for the determination of ion exchange. With the hydroxides (16) no base exchange is possible if the colloidal hydroxides are leached with a solution the pH of which is equal to the isoelectric pH. With other compounds there is base exchange at the isoelectric pH, but it becomes smaller at a pH below the isoelectric pH and increases rapidly above. In a previous paper (16), in order to interpret this remarkable property, it was assumed that the isoelectric point is that point at which the amphoteric colloid has a mininum of the electrovalent form, with hydrions and hydroxyl ions dissociated in an equal degree.

This general review of electrokinetic potentials applies to all the phosphates. Tin hydroxide was found to be isoelectric at pH 3.9, but the substitution of a hydroxyl by a phosphoric acid group increases its acidoid component, and it becomes electronegative at all points of the pH range at which it is precipitated. Calcium and magnesium phosphates are also electronegative at the pH range at which they are precipitated and are within this range functioning as acidoids, for their solubility at a lower pH is so high that they cannot be precipitated in the electropositive condition.

SUMMARY

A series of phosphate precipitates of tin, titanium, iron, aluminum, calcium, and magnesium were prepared, and their cataphoretic behavior and phosphate content at different pH were determined.

Tin and titanium have strong acidic properties and only weakly adsorb phosphoric acid. The compounds, however, are very insoluble and stable in acid solutions, but are dispersed when the pH is increased to about pH 6.0. The phosphates of ferric iron and aluminum are of the same type, but ferric phosphate is more stable in the very acid ranges than is aluminum phosphate. Calcium phosphate is insoluble within a pH range from neutral to strongly alkaline. Magnesium phosphate is less stable than calcium phosphate and more susceptible to both acid and alkaline hydrolysis.

By increasing the pH the phosphate content of the precipitates of tin, titanium, iron, and aluminum is diminished, the hydroxyl replacing the phosphoric acid. Two effects are, however, apparent: the replacement of the phosphoric acid by the hydroxyl groups, and the necessity of having a certain degree of pH in order to obtain the requisite degree of polymerization of the molecules and prevent both acid and alkaline hydrolysis. Since only the pH has been determined in this case, there is no means of deciding the number of hydroxyl groups required to replace the phosphoric acid. On the theory of coördination, however, and in the absence of double bonds, only one hydroxyl group would be required to replace a large group like H_2PO_4 or $HSiO_2$. Definite evidence for this will be published later, as it gives us a means of determining the structure of the internal core in phosphates and silicates.

The significance of electrokinetic potentials and the isoelectric point is discussed.

REFERENCES

(1) BASSETT, H. 1917 The phosphates of calcium. IV. *Jour. Chem. Soc.* 111: 620–642.
(2) BOHR, N. 1913 Constitution of atoms and molecules. *Phil. Mag.* 26: 476–502.
(3) BROWN, I., AND BYERS, H. G. 1932 The fractionation, composition, and constitution of certain colloids derived from the great soil groups. U. S. Dept. Agr. Bul. 319.
(4) BURY, C. R. 1921 Langmuir's theory of the arrangement of electrons in atoms and molecules. *Jour. Amer. Chem. Soc.* 43: 1602–1609.
(5) BYERS, H. G., AND ANDERSON, M. S. 1932 The composition of soil colloids in relation to soil classification. *Jour. Phys. Chem.* 36: 348–366.
(6) DEBYE, P., AND HÜCKEL, E. Theory of electrolytes. *Phys. Ztschr.* 24: 185–206 (1923); 25: 49 (1924).
(7) DENIGÉS, G. 1920 Reaction de coloration extrement sensible des phosphates et des arseniates ses applications. *Compt. Rend. Acad. Sci.* [Paris] 171: 802–804.
(8) FISKE, C. H., AND SUBBAROW, F. 1925 The colorimetric determination of phosphorus. *Jour. Biol. Chem.* 66: 375–400.
(9) GAARDER, T. 1930 Die Bindung des Phosphorsäure im Erdboden. *Meddel. Vestl. Forstl. Forsoksst a.* 4: 4.
(10) LEWIS, G. N. 1923 Valence and the Structure of Atoms and Molecules. Chemical Catalog Co., New York.
(11) LOEB, J. 1924 Proteins and the Theory of Colloidal Behavior. McGraw-Hill, New York.
(12) MCBAIN, J. W. 1920 *Brit. Assoc. Adv. Sci. Rpt. Colloid Chem.* 3: 2–31.
(13) MATTSON, SANTE. The laws of soil colloidal behavior: III. Isoelectric precipitates. Soil Sci. 30: 459–494 (1930); V. Ion adsorption and exchange. Soil Sci. 31: 311–331 (1931); IX. Amphoteric reactions and isoelectric weathering. Soil Sci. 34: 209–240 (1932).
(14) MATTSON, SANTE, AND PUGH, A. J. 1934 The laws of soil colloidal behavior: XIV. Hydrous oxides. *Soil Sci.* 38: 299–313.
(15) MICHAELIS, L. 1926 Electrical phenomena in colloid chemistry. Colloid chemistry, vol. 1. Alexander.
(16) PUGH, A. J. 1934 The laws of soil colloidal behavior: I. Aging of colloids and base exchange. *Soil Sci.* 37: 403–427. II. Ionic exchange with hydroxides. *Soil Sci.* 38: 161–173.
(17) ROBINSON, W. O., AND HOLMES, R. S. 1924 The chemical composition of soil colloids. U. S. Dept. Agr. Bul. 1311.
(18) RUSSELL, E. J. 1932 Soil Conditions and Plant Growth. Longmans Green & Co., London, New York.
(19) SIDGWICK, N. V. 1927 The Electronic Theory of Valency. Oxford University Press, London.
(20) WARD, R. R. 1933 The colorimetric determination of phosphorus in citric acid extracts of soils. *Soil Sci.* 35: 85–97.

A COMPARISON BETWEEN THE PIPETTE METHOD AND THE HYDROMETER METHOD FOR MAKING MECHANICAL ANALYSES OF SOIL

GEORGE JOHN BOUYOUCOS

Michigan Agricultural Experiment Station

Received for publication August 28, 1933

The hydrometer method has been presented (1, 2, 3, 4) as a very rapid, simple, and reasonably accurate method for making mechanical analyses of soil. Since it was first proposed about 7 years ago it has undergone considerable improvement, and in the present form more than 800 persons all over the world both in educational institutions and in industries are using it. Its widespread adoption clearly indicates that there has been a great need for such a method.

Since the pipette method has been adopted by the International Society of Soil Science as the standard method for making mechanical analyses of soil it was decided to compare the hydrometer method with it, and to ascertain to what extent the results obtained by the two methods agree.[1]

The writer first obtained from the United States Bureau of Chemistry and Soils samples of 15 different types of soils together with their mechanical analyses as obtained by the pipette method. These soils were then analyzed by the hydrometer method, and it was found that what the pipette method determined as clay (0.005 mm.), the hydrometer method would determine at the end of 1 hour and what the pipette method determined as fine clay, or colloids (0.002 mm.), the hydrometer method would determine at the end of 2 hours. The data obtained on these soils by the hydrometer method show that the hydrometer method can give results on the clay content of soils that are identical with those obtained by the pipette method.

After this preliminary comparison was made it was decided to test the hydrometer method further by using unknown soils. Accordingly, the United States Bureau of Chemistry and Soils sent the writer 19 different soils without their mechanical analyses. These soils were selected to represent many unusual types and also some types that had unusual particle distribution. It was agreed that the writer was to analyze these soils by the hydrometer method and the United States Bureau of Chemistry and Soils was to analyze the same soils both by the hydrometer method and by the pipette method. After the writer obtained his results, he submitted them to the United States Bureau of Chemistry and Soils without knowing the results it had obtained on the

[1] In this comparative study of the two methods, the writer is indebted to the United States Bureau of Chemistry and Soils for its coöperation and help.

soils by either the pipette or hydrometer method. The results obtained are shown in table 1.

An examination, first, of the results obtained on clay (0.005 mm.) shows that with very few exceptions the two methods agree very well in the different soils. The principal exceptions are soils 12, 17, and 18, but there seem to be definite explanations for these exceptions. Soil 12, for instance, is a soft bauxite with soft concretions which can be easily crushed between the fingers. A mechanical analysis of this soil has not much significance. Soils 17 and 18 contain a

TABLE 1

Comparison between hydrometer and pipette methods

SOILS	CLAY (0.005–000 MM.)			FINE CLAY (0.002–000 MM.)		
	Hydrometer by Bouyoucos	Pipette by U. S. Bur. of Soils	Hydrometer by U. S. Bur. of Soils	Hydrometer by Bouyoucos	Pipette by U. S. Bur. of Soils	Hydrometer by U. S. Bur. of Soils
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1. Marshall silt loam 0–14″	30.7	31.2	28.9	27.2	27.8	27.3
2. Marshall silt loam 14–18″	35.6	36.0	35.4	31.4	32.1	31.4
3. Miami silty clay loam 0–10″	37.0	34.0	35.4	31.3	22.4	31.3
4. Miami silty clay loam 10–24″	69.5	74.8	73.8	63.8	62.6	68.8
5. Soil from Fallon, Nevada	42.1	37.9	39.6	37.2	28.9	35.2
6. Davidson loam 0–9″	35.9	34.0	36.1	31.0	23.5	30.1
7. Davidson loam 9–36″	62.1	59.1	59.3	58.4	49.4	56.4
8. Superior fine sandy loam 12–30″	5.6	6.6	10.0	5.2	5.9	8.1
9. Superior fine sandy loam 30–40″	2.8	3.0	7.5	2.7	2.5	5.5
10. Amarillo silty clay loam 10–20″	47.8	46.5	44.4	43.6	42.2	41.3
11. Amarillo silty clay loam 70–75″	55.00	55.3	54.1	50.2	37.2	48.7
12. Soft bauxite 156–214″	29.8	17.8	x	24.0	11.8	x
13. Houston black clay 0–3″	56.1	60.8	54.5	49.0	43.8	46.7
14. Houston black clay 14–20″	61.3	64.8	59.4	53.8	45.5	50.1
15. Houston black clay 36–50″	54.9	56.6	53.1	48.6	34.6	44.7
16. Cecil clay loam 5–36″	34.7	29.9	33.1	31.6	22.9	30.1
17. Cecil clay loam 36–72″	16.7	9.5	18.2	14.0	7.6	14.2
18. Cecil clay loam 96–112″	11.8	5.2	11.9	9.8	2.7	11.1
19. Sharkey clay soil	68.4	70.5	68.5	63.0	58.5	58.9

considerable amount of mica in the form of flakes, and it is possible that the dispersing machine used in the hydrometer method either broke down the mica into fine material or it dispersed the whole soil more completely than did the shaking machine used in the pipette method.

It is to be noted in soils 8 and 9, which are fine sands, that the writer's hydrometer results agree with those of the pipette method whereas the Bureau's hydrometer results do not agree very closely either with the writer's or with those of the pipette. The reason for this disagreement is that the writer dispersed these sands for 5 minutes only and made a correction for the hydrometer as the directions call for, whereas the United States Bureau of Chemistry and

Soils dispersed these soils for 10 minutes, the same as for clay, and did not make the correction. It has been found advisable to disperse the sands only about 5 minutes because the dispersing machine is so powerful that it tends to break down some of the sand particles, especially those that are not very refractory.

Outside of these three or four special cases the results of the pipette and hydrometer methods agree very well in determining the clay. This agreement is remarkable when it is considered that the hydrometer method completes the determinations in 1 hour as against several days by the pipette method. Where there is any marked disagreement it appears to be due entirely to the question of dispersion and not to the hydrometer instrument itself.

An examination, next, of the results on fine clay (0.002 mm.) shows that the two methods do not agree so closely as they do in the case of the coarser clay. It is also observed that the results obtained by the hydrometer tend to be somewhat higher than those obtained with the pipette. Several explanations may be offered to account for some of these variations. One is that the dispersing machine used in the hydrometer method dispersed the soils more completely than did the shaking machine used in the pipette method. Second, the dispersing reagents employed to stabilize the soil suspensions tend to lose their stabilizing effects in some soils on long standing, and, since in the pipette method the soil suspensions are allowed to stand for 8 hours before the reading is taken as against 2 hours in the hydrometer, it is probable that the settling of the particles in some of the soils was more rapid in the pipette method than in the hydrometer method. Third, in the pipette method only sodium oxalate was used as a dispersing reagent, whereas in the hydrometer method a combination of sodium oxalate and sodium hydroxide was employed, and, as will be shown subsequently, different dispersing reagents affect the dispersion and stabilization of the various soils differently. Fourth, the soils which show variations in the clay content probably contain a very wide particle distribution, and the pipette and hydrometer methods do not measure the same soil particles in such cases. That is to say, when a soil has a very wide distribution of particles, the hydrometer method tends to measure or throw in the class of fine clay some soil material that is coarser than the upper limits of the fine clay. Which one of these explanations is the correct one cannot be said at present. It would seem that they might all contribute in causing the variations in the results but in different degrees, depending upon the soil.

In connection with the disagreement that is exhibited by the results from pipette and hydrometer methods in some soils in table 1, it will now be of much interest and significance to study the disagreement that is revealed within results by the pipette method itself when used by different investigators to analyze the same soils by the same procedure.

This information is contained in the report (6) of the Second International Congress of Soil Science, held in Russia in 1930. The Soil Congress had a large number of laboratories all over the world do cooperative investigation on

the pipette method. Samples of six different soils were sent to these various laboratories to be analyzed by the pipette method according to the same directions to determine how the results from the different laboratories would compare. The results as reported are shown in table 2.

Table 2 shows that the agreement of the various laboratories on the determination of the clay content of the same soils is distinctly disappointing, especially for an international standard method and when the same standard procedure is followed. On account of this lack of agreement in the results by the different laboratories, one is forced to question the claim that the international pipette method is an absolute and reliable method for the mechanical analysis of soils.

If the hydrometer method could be tested by different laboratories as was the pipette method and the same procedure were followed, it seems reasonably

TABLE 2

Clay (0.002 mm.) as obtained by different laboratories on the same soils by means of the pipette method and following the same procedure

SOILS	LABORATORIES									
	Bangor	Belvedere-straat	Brno	Glen Osmond	Kuala Lumpur	Leningrad	London	Oxford	Rothamsted	Zagreb
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1. Brno, Rednzina	66.5	60.1	64.7	65.0	24.0	69.6	63.8	49.1	68.8	60.3
2. Brno, Alluvial	30.7	29.6	29.1	30.1	34.0	33.0	30.4	27.9	32.1	29.7
3. Budapest-Szik	33.3	33.2	35.6	36.4	36.0	39.0	33.5	26.5	35.5	30.2
4. Zagreb	31.3	29.2	27.6	30.2	34.0		32.0	27.2	33.0	27.6
5. Khartoum-Gezira	51.0	48.3	43.7	58.1	6.0	58.0	61.4	27.4	62.2	41.5
6. Khartoum-Alluvial-Kassala	36.2	32.8	36.7	45.2	34.0	48.1	49.0	33.1	45.6	26.0

assured that the results would agree surprisingly and certainly no such wide variation would occur as shown in table 2. The reason for this is that the hydrometer method is very simple, rapid, well-standardized, free of the personal element of the operator, requires no technique such as the pipette method does, and consequently the results can be easily duplicated.

Because the hydrometer method in its operation does not follow or is not in accord with certain physical laws covering hydrometer behavior, it has been criticized by some. But when the results of tables 1 and 2 are taken into consideration these criticisms are neither warranted nor supported by actual facts. It is important to realize that the error that may be caused by the hydrometer instrument itself is insignificant to the great errors that are caused in some soils by not using the exactly proper reagent to disperse them and to stabilize them. As has been abundantly shown, when ammonia, sodium hydroxide, sodium oxalate, and potassium hydroxide are used for reagents, markedly different

results are obtained in some soils. Here lies probably one of the most important problems in the mechanical analysis of soil, viz., to find the proper dispersing and stabilizing reagent that will work absolutely the same in all soils.

In view of all these facts it would seem, therefore, that on the whole the hydrometer method gives results as good as, if not better than, the pipette method, and for the average individual it will give more reliable results than the pipette method. In addition, the hydrometer method will do the work from thirty to forty times faster than the pipette method with very little effort on the part of the operator.

The hydrometer method has received a very thorough and extensive investigation by the United States Bureau of Public Roads (7) and with certain modifications and refinements this bureau has adopted the hydrometer method as its official method.

The hydrometer method has received constant attention with the idea of improving it. The final procedure as developed up to date for making mechanical analysis of soils by the method is as follows: Add 50 gm. of fine-textured soils or 100 gm. of the sand, based on oven-dry condition, to the dispersing cup (plate 1). Fill the cup with distilled water to about $1\frac{1}{2}$ inches from the top. Add to the contents 5 cc. of a solution of normal sodium silicate or water glass (7) having a hydrometer reading of 36 at 67°F. If the soil is in lumps, sufficient time must be given to slake and to soak. As a matter of fact, it is well to allow all soils to soak for about 15 minutes before dispersing them. The soils should always be air dry, because in the wet condition they do not slake. The soaking can be done in a separate vessel and the material then washed into the cup. Then connect the cup to the stirring motor, and stir the contents for 5 minutes in the case of sands and 10 minutes in the case of all other soils. Those soils, however, which are recognized as difficult of dispersion should be dispersed for 20 to 30 minutes or longer. The sands should not be stirred more than 5 minutes because they seem to undergo abrasion.

Pour and wash the contents into the special cylinder. If 50 gm. of soil are used, fill the cylinder to the lower mark with the hydrometer in it. If 100 gm. of soil are used, fill it to the upper mark with the hydrometer in it. Only distilled water should be used. Then take the hydrometer out, place the palm of one hand on the mouth of the cylinder and shake the contents vigorously, turning the cylinder upside down and back several times. Place the cylinder quickly on the table and note the time immediately. Then at the desired period put the hydrometer in the suspension column, record the reading, and then take it out again. There is a tendency for slight amounts of soil material to settle on the shoulder of the hydrometer, and it is better not to leave it in continuously for all readings. Each time the hydrometer is used it should be clean.

At every hydrometer reading the temperature of the suspension should be measured. Great care must be taken, however, not to disturb too much the suspension column in putting in and taking out the hydrometer and the ther-

mometer. For every 1°F. above or below 67°F. apply a temperature correction of 0.2 graduation on the hydrometer. This temperature correction, however, is only an approximation, as it tends to vary somewhat with extreme concentrations of soil suspensions and also with extreme variations of temperature. Probably the most accurate hydrometer readings are taken near the temperature of 67°F., which is the temperature at which the hydrometer was calibrated in actual soil suspensions. Extreme temperatures such as 100°F. and 50°F. should be avoided. If possible, temperatures should be above 67°F. rather than below. For temperatures above 67°F. the corresponding amount of correction is added to the hydrometer reading, and for temperatures below 67°F. the corresponding amount is subtracted. The corrected hydrometer reading is then divided by the weight of soil taken and multiplied by 100, the result being the percentage of material still in suspension.

The hydrometer method cannot subdivide the sands into their various fractions, but can only determine their combined or total amount. Various experimental tests seem to show that the total combined sands of a soil can be ascertained more accurately by taking a hydrometer reading at the end of 40 seconds. A correct reading can be easily made in this short period except in some organic soils which have a tendency to produce froth on the top of the column after being shaken, in which case a correct hydrometer reading is not always possible. One way to overcome this difficulty is to blow at the froth, which tends to disappear quickly. The determination of the combined sand should be considered only as approximately correct.

The hydrometer was calibrated in actual soil suspensions consisting of an average loam soil. Its readings, therefore, are quite accurate. It was found very difficult to calibrate the range from 0 to 10 gm. per liter, however, and readings in this range are not so accurate as in the rest of the range. In this range readings are about 1 gm. per liter too high. It is advisable, therefore, to subtract 1 gm. per liter from all hydrometer readings below 9.9 gm. per liter before correcting for temperature.

A unique feature of the hydrometer method is the fact that the personal element is reduced to a minimum. One cannot but obtain correct results if one watches for one important thing, namely, the condition of the paddle on the stirring rod. Practically the whole success of the hydrometer method depends upon a complete dispersion of the soil, and a complete dispersion can be obtained only when the paddle on the stirring rod or shaft is in good condition. The paddle that has been used heretofore in the method wears out very easily and becomes flat and small. In this condition its efficiency is practically gone and the soils are not properly dispersed and consequently the results are not correct. In order to eliminate this serious weakness in the method, a new paddle or button has been adopted and placed on the stirring rod. When this paddle becomes worn it can be unscrewed from the shaft and replaced with a new one. This new arrangement, besides providing a paddle that is wear-resistant, also obviates the necessity of having to change the

stirring rod in order to change the paddle as has been the case heretofore. The paddles are very inexpensive and can be changed very frequently. It is strongly urged upon all those who are now using the old stirrer to replace it with the new one shown in plate 1.

Another extremely important point is that the cup should have baffles in it. Without the baffles the soils cannot be dispersed easily.

To calculate the conventional amount of combined sand (1.0–0.05 mm.), silt (0.05–0.005 mm.), and clay (0.005–000 mm.) and the finer clay (0.002–000 mm.) as determined by the hydrometer method, the procedure is as follows:

The corrected hydrometer reading at the end of 40 seconds is divided by the amount of absolute dry soils taken and is multiplied by 100. The result is percentage of material still in suspension at the end of 40 seconds. This percentage is subtracted from 100 and the result is the percentage of material that settled out at the end of 40 seconds, which is supposed to represent all the sand in the soil. The corrected hydrometer reading at the end of 1 hour is also divided by the weight of soil sample and multiplied by 100. The result is percentage of material still in suspension and is considered to be the conventional clay (0.005–000 mm.). The percentage of the conventional silt is obtained by subtracting the clay from 100, and from this result subtracting again the percentage of sand. To obtain the finer clay (0.002 mm.), it is only necessary to divide the correct hydrometer reading at the end of 2 hours by the weight of the soil sample and multiply by 100. The organic matter content and the carbonate content are not determined by the method.

It is thus seen that by means of the hydrometer method almost a complete mechanical analysis of soils can be made in only 1 or 2 hours, with the expenditure of very little time and effort.

From all studies and examinations thus far made, it seems that the hydrometer method is reasonably accurate and reliable on all soils that are properly dispersed and properly stabilized by the reagent. It seems to be especially accurate in the coarse clay fraction (0.005 mm.). In the finer clay portion (0.002 mm.) it may not be so accurate in some soils that have a very large amount of their finer material just slightly above the 0.002-mm. size. In such soils the hydrometer method indicates a larger content of the 0.002-mm. fraction than the pipette method, but the difference may not be very large.

In peats and mucks the hydrometer method is not very reliable, first, because these materials are almost impossible to disperse, and second, because they have a smaller specific gravity and the hydrometer was calibrated on average normal loam soils. The method, however, seems to be quite accurate on mineral soils containing a moderately high organic matter content, provided the latter is well decomposed and is completely dispersed. As previously shown (5), mineral soils containing a very high organic matter content in an incompletely decomposed state should be first treated with hydrogen peroxide. Mineral soils containing no, or only small amounts of, well-decomposed organic matter need not be treated with hydrogen peroxide.

It is advisable to wash very alkaline soils before using them for analysis, or a correction should be applied for the salts if present in appreciable amounts.

By taking hydrometer readings continuously or every so often, a complete distribution curve of size particles of soils and their respective amounts can be readily and very reliably obtained.

The hydrometer method, therefore, would seem to give most, if not all, of the essential information required for all practical purposes, and because of its great rapidity, simplicity, and reasonable accuracy, it should meet a great need.

SUMMARY

With the coöperation of the United States Bureau of Chemistry and Soils, the hydrometer method for the mechanical analysis of soils was examined and compared with the pipette method.

It was found that what the pipette method determines as coarse clay (0.005 mm.) the hydrometer would determine at the end of 1 hour, and what the pipette method determines as fine clay (0.002 mm.) the hydrometer method would determine at the end of 2 hours.

The results obtained show that the two methods agree exceptionally well on the determination of the coarser clay (0.005 mm.). On the determination of the fine clay (0.002 mm.) they do not agree very closely on some soils but on the majority of soils they agree satisfactorily. The disagreement between the two methods in some soils seems to be due to differences in dispersion.

A new stirrer is now employed in place of the original one. In this new stirrer the paddle is made of hard steel and when it becomes worn, it can be unscrewed from the stirring rod and replaced with a new one.

On account of its great simplicity and rapidity, and its reasonable accuracy, it seems that the hydrometer method has many distinct advantages over all other methods.

On account of the many inquiries received as to the price of the hydrometer method outfit, and where it may be obtained, the following information is given:

The dispersing machine and cup, which cost about $22, are handled by the Hamilton Beach Company, Racine, Wisconsin.

The hydrometer and cylinder, which cost about $5, are handled by the Taylor Instrument Company, Rochester, New York.

REFERENCES

(1) Bouyoucos, G. J. 1926 The hydrometer as a new and rapid method for determining the colloidal content of soils. *Soil Sci.* 23: 319–330.

(2) Bouyoucos, G. J. 1928 The hydrometer method for studying soils. *Soil Sci.* 25: 365–369.

(3) Bouyoucos, G. J. 1928 The hydrometer method for making a very detailed mechanical analysis of soils. *Soil Sci.* 26: 233–238.

(4) BOUYOUCOS, G. J. 1930 A comparison of the hydrometer method and the pipette method for making mechanical analyses of soils. With new directions. *Jour. Amer. Soc. Agron.* 23: 747–751.

(5) BOUYOUCOS, G. J. 1932 Studies on the dispersing procedure used in the hydrometer method for making mechanical analysis of soils. *Soil Sci.* 33: 21–26.

(6) NOVAK, V. 1932 Vorbehandlung der Bodenproben zur mechanischen Bodenanalyze. *Proc. Second Internatl. Cong. Soil Sci.* 1 (Comn. 1): 14–39.

(7) THOREEN, R. C. 1933 Comments on the hydrometer method of mechanical analysis. *Public Roads* 14: 93–105.

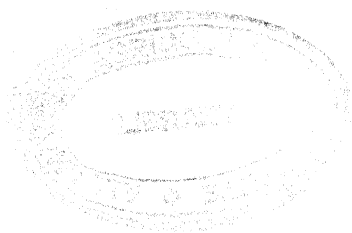


PLATE 1

THE DISPERSING MACHINE, SPECIAL CUP, SPECIAL CYLINDER, AND SOIL HYDROMETER

The paddle is screwed to the stirring rod and can be replaced when it becomes worn





LIBRARY

THE DETERMINATION OF PHOSPHATE AVAILABILITY IN CALCAREOUS SOILS BY ELECTRODIALYSIS

W. T. McGEORGE

Arizona Agricultural Experiment Station

Received for publication November 21, 1933

It is possible to make a fairly reliable estimate of phosphate availability in many soils by one or several of the methods now in use. The limit of interpretation which can be made from the data is largely a matter of soil type, and since most chemical methods involve the use of acid solvents they are of limited or doubtful value for calcareous soils. By electrodialysis it is possible to extract the soluble, and to a large extent the available, phosphate with less interference in calcareous soils than in non-calcareous types. Phosphate is present in calcareous soils largely as carbonato-apatite. In the presence of an excess of CO_3 ion and solid phase $CaCO_3$ the solubility of this compound is reduced to zero, whereas it is appreciably soluble at slight concentrations of hydrogen ions, such as that produced by free CO_2 in the soil solution.

In a recent study of electrodialysis (3), conducted in this laboratory, it was shown that soil phosphate is readily dissolved by this procedure and that there is a close relation between the rate of electrodialysis and the performance of the soils in plant tests. In fact, over a definite period of time the specific solution rate of phosphate is a remarkably constant value for each soil. Absorption of phosphate by plants takes place largely or entirely as the H_2PO_4 ion, which is the dominant ion formed by ionization of phosphates at reactions below pH 6.8. It is of interest in this connection that the most satisfactory chemical methods of determining availability are those in which slightly acid solvents, preferably buffered at a low hydrogen-ion concentration, are utilized. This condition can be accomplished, in calcareous soils, only by electrodialysis. When a calcareous soil is electrodialyzed in a three-chamber cell there is a rapid reduction in pH of the soil-water mixture in the middle chamber. In spite of the excess of $CaCO_3$ present the pH can be reduced to pH 4.0 even though the soil-water mixture is continuously agitated with a stream of air. This indicates that electrodialysis closely imitates the plant roots in extracting phosphate from soils, because within the root-soil contact zone the root itself creates a low pH by secretion of CO_2. It also imitates the buffered dilute acid solutions used to dissolve available phosphate from non-calcareous soils.

In our investigations phosphate (3) was determined in the anode solution by the molybdenum-blue method, and it was found that a current of 0.2 ampere was best suited for yielding determinable amounts. It was observed that regardless of the amount of current flowing, when 10 gm. of soil was used, and

provided the electrodialysis was continued long enough, the curve obtained, by plotting time against phosphate extracted, became practically horizontal. This suggested that the amount of phosphate which can be removed from a soil by electrodialysis is a constant for any amperage, and we therefore extended our studies along this line.

EXPERIMENTAL

Phosphate removed by constant amperage and variable weight of soil

The apparatus used was essentially that of Mattson, as described in a previous publication, and is similar to that used by Harper (2), except that we used 1 liter of water in each of the electrode chambers and 100 cc. in the middle chamber. A cathode of sheet copper, 7 x 10 cm., and an anode of platinum gauze, 5 x 12.5 cm., were used. As a source of current a 2–12 volt rectifier was attached to the lighting circuit. Adjustable resistance was inserted to maintain a constant flow of current at 0.2 ampere, and electrodialysis was continued until the analysis of the solution in the anode chamber showed that no further phosphate was being removed from the soil. This required 4 to 8 hours.

TABLE 1

PO_4 removed from 1, 2.5, 5, 10 gm. portions of soil by .2 ampere

Expressed as milligrams PO_4 per 10 gm. soil

SOIL NO.	10 GM. SOIL	5 GM. SOIL	2.5 GM. SOIL	1 GM. SOIL
1	17.4	17.0	18.0	17.5
2		12.0	14.8	15.0
3	4.0	5.0	6.0	5.0
4	6.1	8.0	8.0	
5	12.0	11.6	11.8	12.0
6	7.0	6.8	7.2	8.0

The soils selected for this experiment were all calcareous soils. The results obtained are given in table 1 and are calculated to a basis of milligrams PO_4 per 10 gm. soil, although the actual amounts of soil used were 1, 2.5, 5, and 10 gm.

These data show that, provided the amount of current flowing is a constant, all soils contain a definite amount of phosphate which can be brought into solution when they are subjected to electrodialysis.

Phosphate removed by variable current from a definite weight of soil

Having shown that the amount of phosphate which can be removed from soils by 0.2 ampere is a constant for every soil, we next varied the current and kept the weight of soil constant. Two grams of soil was used in all cases and the amount of current varied between 0.1 and 1.0 ampere, a rectifier being used for the small flow of current and a motor generator for the greater flow. As in

the preceding experiment, the electrodialysis was continued until the phosphate concentration of the anode chamber had reached a constant. From the group of calcareous soils studied two representative samples are selected, one of which is low and the other high in electrodialyzable phosphate. The amounts of phosphate extracted by electrodialysis at several variations in amperage are given in figure 1.

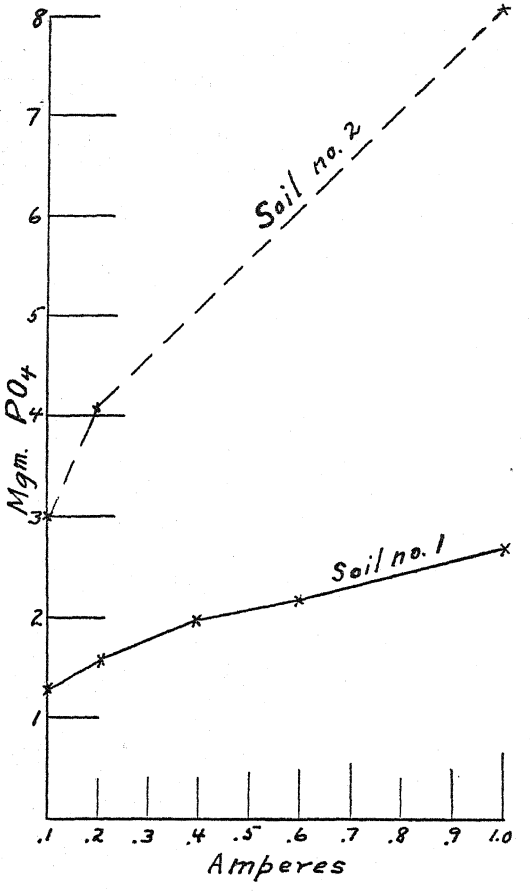


FIG. 1. TYPICAL EXAMPLES OF THE EFFECT OF AMPERAGE ON PHOSPHATE EXTRACTED BY ELECTRODIALYSIS FROM A POOR SOIL, NUMBER 1, AND A GOOD SOIL, NUMBER 2

This experiment shows that the amount of phosphate which can be withdrawn from a soil by electrodialysis depends upon the amperage, and that flow of current must be carefully controlled if the analyses are to be comparative. There is evidence that the rate of increase in solubility with increase in flow of current may serve as a measure of the supplying power of the soil. Soil No. 1 shows a low initial solubility at 0.1 ampere and a low

measured by increase in flow of current. In this soil the amount of phosphate dissolved by 1.0 ampere is twice that removed by 0.1 ampere. Soil No. 2, which is well supplied with available phosphate, shows a higher initial yield at 0.1 ampere and a greater increase as the flow of current is increased up to 1.0 ampere. It is believed that the phosphate removed by 0.1 ampere represents the liquid phase and the easily soluble solid phase phosphate, such as di-calcium phosphate, following which the carbonato-apatite is extracted. This suggestion is based on the fact that we obtained no increase in amount of electrodialyzable phosphate by grinding these same two soils in a ball mill for 100 hours, showing that fineness of division or size of soil particles is not related to the rate at which phosphate can be removed from soils by this procedure.

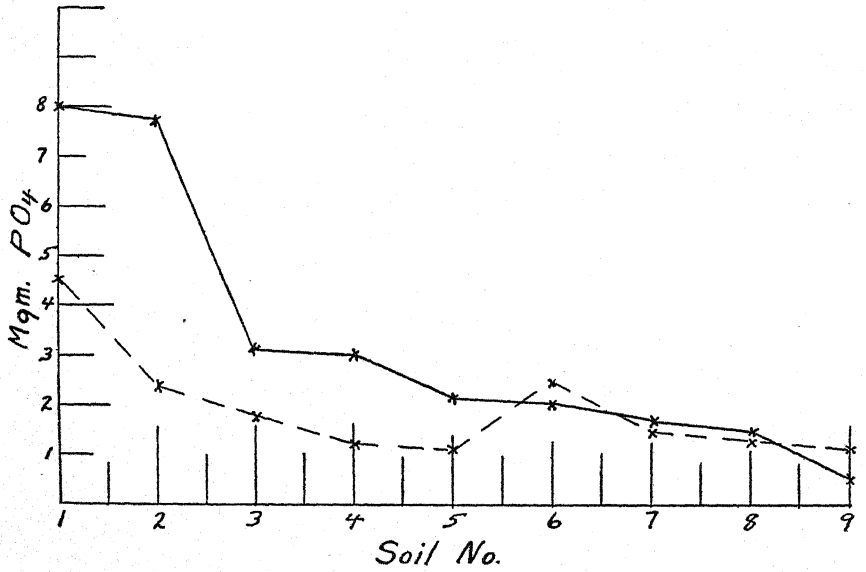


FIG. 2. RELATION BETWEEN NEUBAUER VALUE (SOLID LINE), MILLIGRAMS PO_4 REMOVED FROM 100 GM. SOIL BY 100 RYE PLANTS, AND MILLIGRAMS PO_4 (BROKEN LINE) EXTRACTED FROM 2 GM. SOIL BY ELECTRODIALYSIS WITH 0.2 AMPERE FLOW OF CURRENT

Relation of electrodialyzable phosphate to Neubauer values

The preceding data, together with our previous investigations (3), have led us to believe that for calcareous soils it is not necessary to use a current of more than 0.1 ampere, or 0.2 ampere at the most, and that a 2 gm. sample of soil is sufficient to yield readily determinable amounts of phosphate. On this basis nine calcareous soils were selected. The amount of phosphate withdrawn by a current of 0.2 ampere from 2 gm. of soil was determined, as was also the Neubauer value. These data are shown graphically in figure 2. A rather close correlation between Neubauer values and the amount of available phosphate as determined by electrodialysis is demonstrated.

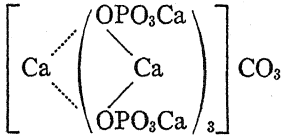
DISCUSSION

The soils used throughout these experiments have been calcareous soils, and therefore the method suggested is believed to be applicable only to such types, which, however, are the most prevalent types in the irrigated valleys of the Southwest. In other of our investigations (3, 4) we have used non-calcareous types as well as a number of phosphate minerals and noted wide variations in their rate and ease of dialysis. This is especially true in comparisons of calcium and iron or aluminum phosphates and the phosphate ions adsorbed by positive and negative colloids. Except for the ferrous phosphate, vivianite, the iron and aluminum phosphates do not yield their phosphate readily to solution when subjected to electrodialysis. Therefore electrodialyzable phosphate must be derived in most part from calcium and magnesium compounds, to a small extent from organic phosphate (4), and to a limited extent from phosphate adsorbed by the soil colloids. Since yield of phosphate to electrodialysis depends upon solubility and adsorption forces, the equilibrium, which represents maximum solubility for each different amperage, will vary with the magnitude of these forces in the soil. Also, since solubility reactions proceed toward equilibrium, if the products of the reaction are removed from the middle chamber of the cell as they are in electrodialysis, the solubility will proceed to the limit of the conditions established for the cell, which in this case is the amount of current flowing. It seems reasonable to assume that since the amount of phosphate in the soil solution at any one time is a function of the solubility of the chemical forms present and the nature of the soil colloids, particularly the charge upon the colloid, these factors directly determine the supplying power of the soil. Therefore, if electrodialysis measures these processes it must closely imitate the existing forces which function in the feeding operations of the plant.

In discussing the value of electrodialysis too much emphasis cannot be placed upon the limitation which variation in soil type places upon the process. Our own work suggests the separation of soils into three groups according to the reaction of the soil; namely, acid soils, neutral soils, and alkaline soils. Since iron and aluminum phosphates, as well as the phosphate absorbed by hydrated oxides of iron and aluminum, do not react readily to electrodialysis (4) when a 2 gm. sample is subjected to a current of 0.2 ampere, it should be necessary to use in such soils a greater flow of current as well as a larger sample of soil. Even then it is doubtful whether appreciable solution of phosphate can be obtained. Iron and aluminum phosphates are least soluble at reactions between pH 4.0 and 7.0, and since the soil in the central chamber of the cell is maintained at low pH it is self-evident that conditions in the cell will not promote increased solubility of phosphate during electrodialysis of acid soils. Alkaline calcareous soils are best suited to this method because their phosphate is largely present as carbonato-apatite. The solubility of this compound is greatly increased when the pH of the soil is lowered below pH 7.0, and thus far not a single calcareous soil has been met which has not yielded readily

determinable amounts of phosphate when 2 gm. of soil are electrodialyzed at 0.2 ampere. The third group of soils, those within the immediate range of pH 7.0, probably contain all the aforementioned forms of phosphate but would doubtless require a larger sample of soil and possibly a stronger flow of current for electrodialysis than an alkaline calcareous soil.

It is of interest in this connection to compare some of our data with those of Harper (2), whose studies on electrodialysis of soils showed that with few exceptions soils yielding less than 30 p.p.m. phosphorus (equivalent to 90 p.p.m. PO_4) were deficient, that is, gave response to phosphate fertilization. This is equivalent to 0.9 mgm. PO_4 per 10 gm. soil. When this is compared with 7.0 mgm. PO_4 per 10 gm. soil for a calcareous soil (soil No. 6, table 1), which gives marked response to phosphate fertilization, it is difficult for one not familiar with alkaline calcareous soils to conceive of a deficiency. This comparison is inserted merely to emphasize the influence of soil type on rate of dialysis and then, in turn, the relation of this rate to availability as measured by plant behavior. The reason for poor availability in calcareous types is best illustrated by the formula for carbonato-phosphate which is given by Gassmann and Werner (1) as



It may be readily understood from this formula why the solubility of this compound is reduced to zero in the presence of solid phase $CaCO_3$ and an alkaline reaction, and why the presence of an excess of CO_2, or the presence of H ions, increases the solubility.

There is still another difference between calcareous alkaline soils and non-calcareous types which is important and which may influence the amount of phosphate obtained by electrodialysis. Reference is made to the conductivity or the capacity of different soils to carry a flow of current. An alkaline calcareous soil will conduct a flow of 1.0 ampere very readily and will require little change in resistance throughout an 8 hour period, whereas a non-calcareous soil will carry 1.0 ampere only for a very short initial period, after which it cannot be maintained above 0.2 ampere even when the current is increased to 60 D. C. volts. Although the amperage may be raised by addition of $CaCO_3$ to the middle chamber, the effect is only temporary and has no influence on the amount of phosphate brought into solution. The steadiness of current flow in calcareous soils is a point in favor of the adaptability of the electrodialysis method to this type.

CONCLUSIONS

Electrodialysis is admirably suited to the determination of available phosphate in alkaline calcareous soils because the pH of the soil-water mixture

can be reduced to as low as pH 4.0 in spite of the excess of $CaCO_3$ which is present.

The percentage of phosphate which can be extracted by electrodialysis is a constant value for every soil regardless of the amount of soil used. On the other hand, the value varies with the amount of current flowing, and amperage must be controlled by adjustable resistance to produce comparative results.

There is a close relation between Neubauer values and amount of phosphate removed from soils by electrodialysis.

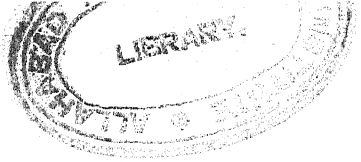
REFERENCES

(1) GASSMANN, Z. 1928 The artificial preparation of the main constituent of bones and teeth. *Ztschr. Physiol. Chem.* 177: 62.

(2) HARPER, H. J. 1933 The easily soluble phosphorus content of soil as determined by electrodialysis, extraction with dilute acid solutions, and crop response to fertilization. *Soil Sci.* 35: 1–16.

(3) MCGEORGE, W. T. 1932 Electrodialysis as a measure of phosphate availability in soils, and the relation of soil reaction and ionization of phosphates to phosphate assimilation. *Ariz. Agr. Exp. Sta. Tech. Bul.* 38: 593–630.

(4) MCGEORGE, W. T., AND BREAZEALE, J. F. 1932 Studies on iron, aluminum, and organic phosphates and phosphate fixation in calcareous soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 40: 59–111.



THE ARSENIC CONTENT OF SOILS

J. E. GREAVES[1]

Utah Agricultural Experiment Station[2]

Received for publication December 2, 1933

Large quantities of arsenic are used annually in the spraying of fruit, sugar beets, alfalfa, cotton, and other crops. Arsenic is also being used to a limited extent for killing weeds. Most of this arsenic finds its way into the soil. In addition to this, Kunkel (19) found arsenic in many rocks and waters. Later investigators (2, 3, 8, 23, 25) have shown it to be present in appreciable quantities in the surface and underground waters of some regions. Czapek (6) states that traces of arsenic are nearly always present in soil. It has been found so frequently in soil by some investigators (24, 28) that they have come to refer to it as a "normal" constituent of "soil." Herzfeld and Lange (18) found arsenic in certain raw sugars and traced it to the limestone which had been used in the manufacture of the sugar. Headden (17) found some virgin prairie soils relatively rich in arsenic; this is in accord with the findings of the author (10) who found arsenic in virgin soil to the extent of 4 p.p.m. It did not result from smelter smoke or similar sources, and, as reported by Headden in his investigations, was derived from the decay of native rock.

Arsenic not only occurs in soil but, because of methods of application and fixation by bases, tends to accumulate in the surface soil (20, 24, 28). Headden (16) found arsenic in some cultivated orchard soils to the extent of 138 p.p.m. and he believes that in many places the accumulation is so great as to render it injurious to vegetation. Cooper and his co-workers (5) found that the application of small quantities of arsenic to light soils decreased yields of cotton and cowpeas. On the other hand, Stewart and Smith (26) produced no injury to peas, radishes, wheat, beans, and potatoes until large quantities of soluble arsenic were applied to a highly calcareous soil. Francois (7) considers that there is little danger of the earth becoming unfit for vegetation from the proper use of insecticides, which is in keeping with the conclusions of Ball and his co-workers (4). Grunner (14), who found arsenic to the extent of from 0.026 per cent to 1.426 per cent in the Reichensterm soil, is not so optimistic. Priezker (22), in the analysis of a soil near Basel, Germany, states that it contained from 0.09 to 0.168 per cent of arsenic trioxide, which was conspicuous for its poisonous effect on vegetation and animals.

[1] Bacteriologist and chemist.

[2] Contribution from department of bacteriology and chemistry. Publication authorized by director, November 26, 1933.

The study of arsenic-decomposing fungi by Thom and Raper (27) and their claim that the fungi will keep down the concentration of arsenic in the soil give to the subject a brighter outlook, for if arsenic does not accumulate in soil the likelihood of injury is slight. Moreover, the quantity of arsenic in the soil does not determine its toxicity, but rather its toxicity is determined by its solubility, which is dependent upon the chemical and biological properties of the soil.

It is evident from this brief review of the literature that the quantity of arsenic accumulating in a soil and its toxicity to plant life have not been fully determined; yet the solution is of vital economic importance to permanent agriculture. Therefore, this investigation has been conducted in the hope that some light might be shed on the quantity of arsenic occurring in some soils, its solubility, and the factors influencing its solubility. Total arsenic and water-soluble arsenic, as well as the soluble salt content of some fifty widely different soils, are reported in this paper.

METHODS

The total arsenic was obtained by extracting the soil with nitric and sulfuric acid and determining the quantity of arsenic by the Marsh method, modified so that iron did not interfere (9). The water-soluble arsenic and soluble salts were determined by extracting for eight days 500 gm. of soil with 2,000 cc. of CO_2-free water. The arsenic was determined by the Marsh and the soluble salts by standard methods. All determinations were made in triplicate and results averaged. In order to economize on space, only the summarized results are given. These bring out the principal facts, but it must be borne in mind when interpreting them that the maximum and minimum as given in the tables for total arsenic, soluble salts, carbonates, chlorides, sulfates, nitrates, organic nitrogen, and calcium do not necessarily correspond for the specific soil for maximum and minimum water-soluble arsenic.

The total arsenic of the soil varies from 7.2 to 367.2 pounds of arsenic per acre-foot. An acre-foot was taken as 3,600,000 pounds. Eight of the soils tested carry over 200 pounds per acre-foot of arsenic, and over one-third of them contained more than 100 pounds of arsenic per acre-foot of soil. Thus, in some of the soils a remarkably large quantity of arsenic has accumulated. This is evidence that arsenic is accumulating in these soils; unfortunately, the quantity of arsenic which has been applied to these soils is not known. Consequently, it has been impossible to check the theory of Thom and Rogers that some molds change soil arsenic to arsine and hence limit its accumulation in soil. It is, however, evident from these results (table 1) that large quantities of arsenic may, and at times do, accumulate in some soils.

Even the arsenic occurring in these soils may not be injurious to microbial and plant life, since it has been shown that from 60 to 100 pounds per acre-foot of arsenic as lead arsenate may stimulate microbial activity in a highly calcareous soil, and it requires from 600 to 700 pounds to reduce bacterial activities

greatly (12). However, small quantities in a light soil, low in calcium and iron, and especially when the arsenic is applied as Paris green or an arsenite, may produce marked injurious effects (11, 12, 13). The same results hold for some higher plants. Stewart and Smith (26) failed to injure plants by applying 100 pounds of disodium arsenate to an acre of highly calcareous soil, whereas Cooper and his co-workers (5) injured cotton and cowpeas with quantities as low as 50 pounds per acre when applied to light soil. In neither case is the quantity of water-soluble arsenic actually occurring in the soil given.

The water-soluble arsenic in some of the soils under consideration is appreciable, varying from 0.7 to 31.9 pounds per acre-foot of soil. Four soils carry over 20 pounds per acre-foot of water-soluble arsenic and 18 contain 9 pounds or over.

TABLE 1

Summary of water-soluble arsenic and total arsenic found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	TOTAL ARSENIC
Maximum	31.9	367.2
Mean	8.5	101.6
Minimum	0.7	7.2
Coefficient of Correlation	0.4214 ±0.0762	

The correlation coefficient between water-soluble arsenic and total arsenic has been calculated (21) according to the formula

$$r = \frac{(x_1 y_1)}{N\sigma_1 \sigma_2}.$$

where r is the correlation between the two variables x and y, of which σ_1 and σ_2 are the respective deviations and N is the number of pairs of variables; x_1 and y_1 are deviations from the means of x and y, respectively.

The probable error has been calculated by the formula:

$$\text{P.E.} = \frac{.67449\ (1 - r^2)}{N}$$

The number of determinations used in the calculations is probably too limited for most satisfactory results, but the individual determinations are the averages of three determinations, hence are based on 150 determinations. However, the results must not be considered as final but rather indicative of what may be expected, subject to modification when more extensive work can be done.

The correlation between total arsenic and water-soluble arsenic = 0.4214 ±

0.0762, thus indicating that the water-soluble arsenic is a function of the total arsenic in the soil. However, there are cases in which the total is high and the water-soluble arsenic low and vice versa, thus indicating that factors other than mere quantity of arsenic in soil govern its solubility. Stewart and Smith (26) found the solubility of lead arsenate to be greatly increased by many common salts when these are present in the aqueous solvent, but sulfates and nitrates apparently do not increase materially the solvent power of water for lead arsenate. Acid salts and those which hydrolize with an alkaline reaction markedly increase the solvent action of water on lead arsenate. Hence, one may expect the solubility of soil arsenic to be a function of the chemical nature of the soil which is reflected by the soil constituents held in the liquid phase.

TABLE 2

Summary of water-soluble arsenic and total water-soluble salts found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	TOTAL WATER-SOLUBLE SALTS
Maximum	31.9	45,000
Mean	8.6	8,511
Minimum	0.72	1,732
Coefficient of Correlation	−0.0274 ±0.0961	

TABLE 3

Summary of water-soluble arsenic and sodium chloride found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	SODIUM CHLORIDE
Maximum	31.9	3,024.0
Mean	8.5	405.7
Minimum	0.72	18.0
Coefficient of Correlation	0.0907 ±0.0954	

Water-soluble salts of these soils varied from 1,732 to 45,000 pounds per acre-foot (table 2). All except four of these soils had less than 21,000 pounds of soluble salts; the four soils carrying quantities greater than 21,000 pounds contained from 3 to 15 pounds per acre of soluble arsenic, whereas another soil containing 6,000 pounds per acre of total soluble salts carried 33 pounds per acre of soluble arsenic. The value of r in this series = 0.02739 ± 0.0961, indicating that it is not the total quantity of soluble constituents within the soil but the predominance of specific chemical compounds which governs the solubility of the arsenic.

The sodium-chloride content of the soils varied from 18 to 3,024 pounds per acre-foot of soil (table 3), all except four containing less than 1,000 pounds per

acre-foot. The soils carrying the largest quantities of soluble arsenic are often those which contain the smallest quantities of sodium chloride. In this series $r = 0.0907 \pm 0.0954$.

All soils used contained appreciable quantities of sodium carbonate, the highest carrying 3,831 pounds per acre-foot (table 4). Probably sodium car-

TABLE 4

Summary of water-soluble arsenic and sodium carbonate found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	SODIUM CARBONATE
Maximum	31.9	3,831
Mean	8.6	1,451
Minimum	0.72	579
Coefficient of Correlation	0.1379 ±0.0927	

TABLE 5

Summary of water-soluble arsenic and sulfates found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	SULFATES
Maximum	31.9	2,372.0
Mean	7.8	500.0
Minimum	0.72	64.8
Coefficient of Correlation	−0.0592 ±0.1024	

TABLE 6

Summary of water-soluble arsenic and calcium oxide found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	CALCIUM
Maximum	31.9	6,290
Mean	8.6	1,618
Minimum	0.72	126
Coefficient of Correlation	0.0523 ±0.0960	

bonate increases slightly the solubility of arsenic, whereas calcium, iron, and magnesium carbonate would depress the solubility. The correlation coefficient in this series is only 0.1379 ± 0.0927.

Thirty of the soils contained 1,000 pounds or less of sulfates per acre-foot (table 5). Apparently, sulfates have little effect on the solubility of the arsenic, for the value of r was found to be -0.0592 ± 0.1024.

Most of the soils contain appreciable quantities of calcium, which one would expect to decrease the solubility of the arsenic, since arsenic is found to be less toxic to plants and soil microörganisms in a calcareous soil than in a non-calcareous soil (table 6). Usually these soils have the smallest quantities of water-soluble arsenic. The value of r in this series was found to be $= 0.0523 \pm 0.0960$. Some of these soils carry large quantities of nitrates, which apparently increase the solubility of the arsenic, for r was found to equal 0.2781 ± 0.0939 (table 7).

The organic nitrogen content of the soils was usually rather low, with no evidence that it tends to increase the solubility of the arsenic (table 8). At times

TABLE 7

Summary of the water-soluble arsenic and nitrates found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	NITRATES
Maximum	31.9	1,783
Mean	8.5	752
Minimum	0.72	130
Coefficient of Correlation	0.2781 ±0.0939	

TABLE 8

Summary of the water-soluble arsenic and organic nitrogen found in 50 soils

Pounds per acre

	WATER-SOLUBLE ARSENIC	NITROGEN OTHER THAN NITRATES
Maximum	31.9	12,343
Mean	8.5	4,529
Minimum	0.72	1,099
Coefficient of Correlation	0.0542 ±0.0933	

the soils having the largest quantity of organic nitrogen contained the smallest quantities of water-soluble arsenic.

SUMMARY

Fifty orchard soils, varying widely in chemical, physical, and biological properties, were analyzed for total arsenic, water-soluble arsenic, and various soluble salts. Total arsenic varied from 7.2 to 367.2 pounds per acre-foot of soil, thus indicating that large quantities of arsenic may accumulate in soil. The water-soluble arsenic varied from 0.7 to 31.9 pounds per acre-foot of soil. It is probable that the toxicity of arsenic to plants and to soil microörganisms is governed by the solubility of the soil arsenic. Hence, the correlation be-

tween various soluble salts and soluble arsenic in the soil was determined. The limited number of soils analyzed, together with the high probable error, makes the conclusions merely tentative. No correlation was found to exist between water-soluble arsenic and total soluble salts, sodium chloride, sulfates, calcium carbonate, and organic nitrogen of the soil. A slight correlation was found to exist between the water-soluble arsenic and sodium carbonate and nitrate.

REFERENCES

(1) ALBERT, W. B., AND ARNDT, C. H. 1931 Concentration of soluble arsenic as an index of arsenic toxicity to plants. *S. C. Agr. Exp. Sta. Ann. Rpt.* 1931: 47–48.

(2) BADO, A. A. 1917 Presence of vanadium and arsenic in the subterranean waters of Belle-Ville (Cordoba), Argentine. *An. Soc. Cient. Argentina* 84: 284–96 (*Chem. Abs.* 12: 1324).

(3) BADO, ATILO, AND ZANETTA, A. J. 1921 The percentage of vanadium and arsenic in waters from some wells in the city of Buenos Aires. *An. Assoc. Quim. Argentina* 9: 24–25 (*Chem. Abs.* 21: 2946).

(4) BALL, E. D., TITUS, E. G., AND GREAVES, J. E. 1910 The season's work on arsenical poisoning of fruit trees. *Econ. Ent.* 3: 187–197.

(5) COOPER, H. P., *et al.* 1931 Effect of calcium arsenate on the productivity of certain soil types. *S. C. Agr. Exp. Sta. Ann. Rpt.* 1931: 28–37.

(6) CZAPEK, FRIEDRICH 1913 Biochemie der Pflanzen, Aufl. 2. Gustav Ficher, Jena.

(7) FRANCOIS, L. 1912 Arsenic compose et destruction de parasite. *Rev. Chim. Indus.* 23: 124.

(8) GOY, S., AND GOY, R. W. 1927 Über den gehalt von Ost Preussichen Gewassern an Arsen. *Land. Angew. Chem.* 40: 945–948.

(9) GREAVES, J. E. 1913 Some factors influencing the quantitative determination of arsenic in soils. *Jour. Amer. Chem. Soc.* 35: 150–156.

(10) GREAVES, J. E. 1913 The occurrence of arsenic in soils. *Biochem. Bul.* 2: 519–523.

(11) GREAVES, J. E. 1913 Some factors influencing ammonification and nitrification in soils. I: Influence of arsenic. *Centbl. Bakt.* (II) 39: 542–560.

(12) GREAVES, J. E. 1916 Stimulating influence of arsenic upon the nitrogen-fixing organisms of the soil. *Jour. Agr. Res.* 6: 389–416.

(13) GREAVES, J. E., AND CARTER, E. G. 1924 Influence of sodium arsenite on microflora of soil. *Bot. Gaz.* 77: 63–72.

(14) GRUNNER, H. 1910 Die Arsen haltigen Boden von Reichenstein. *Landw. Jahrb.* 40: 517.

(15) HEADDEN, W. P. 1908 Arsenical poisoning of fruit trees. Colo. Agr. Exp. Sta. Bul. 131.

(16) HEADDEN, W. P. 1909 Arsenical poisoning of fruit trees. *Jour. Econ. Ent.* 2: 239–245.

(17) HEADDEN, W. P. 1910 Notes on some mineral springs. *Proc. Colo. Sci. Soc.* 9: 259–272.

(18) HERZFELD, A., AND LANGE, A. E. 1911 The cause of the presence of traces of arsenic in raw sugars. *Ztschr. Zukerindus.* 61: 365–375 (*Chem. Abs.* 5: 2342).

(19) KUNKEL, ADAM J. 1905 So-called normal arsenic. *Ztschr. Physiol. Chem.* 44: 511–529. (*Jour. Chem. Soc.* 88, Abs. 542.)

(20) MCGEORGE, W. T. 1915 Fate and effect of arsenic applied as a spray for weeds. *Jour. Agr. Res.* 5: 459–463.

(21) PEARL, RAYMOND 1923 Introduction to Medical Biometry and Statistics. W. B. Saunders Company, Philadelphia.

(22) PRITZKER, J. 1923 Arsenic as a natural poison in a Swiss cultivated soil. *Technik and Indus.* and *Schweiz. Chem. Ztg.* 17: 185–188.

(23) REICHERT, F., AND TRELLES, R. A. 1921 Iodine and arsenic in the underground waters of the Argentine Republic. *An. Assoc. Quím. Argentina* 9: 80–85 (*Chem. Abs.* 15: 3352).

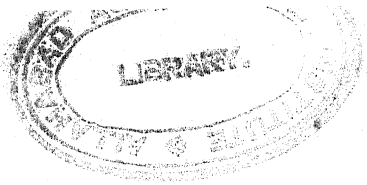
(24) REICHERT, F., AND TRELLES, R. A. 1921 Presence of arsenic as a normal constituent of cultivated soils. *An. Assoc. Quím. Argentina* 9: 89–95 (*Exp. Sta. Rec.* 46: 814).

(25) REICHERT, F., AND TRELLES, R. A. 1921 Arsenic and iodine in soils and subterranean water in Argentina. *Rev. Facult. Agron.* 3 (pt. 3): 281–287 (*Chem. Abs.* 17: 2625).

(26) STEWART, J., AND SMITH, E. S. 1922 Some relations of arsenic to plant growth. *Soil Sci.* 14: 111–126.

(27) THOM, CHARLES, AND RAPER, K. B. 1932 The arsenic fungi of Gosio. *Science* 76: 548–550.

(28) ZUCCARI, GINO 1913 Sulla prisenza dell' arsenico come elemento normale nelle terre. *Gaz. Chim. Ital.* 43: 398–403.



FUNCTIONAL RELATIONSHIPS BETWEEN SOIL PROPERTIES AND RAINFALL

HANS JENNY AND CHESTER D. LEONARD

University of Missouri[1]

Received for publication December 8, 1933

The study of functional relationships between soil properties and soil forming factors permits the establishment of numerical laws of soil formation and will serve as a basis for the formulation of quantitative theories. Approaching soil formation from the viewpoint of a dynamic chemical system one would postulate that in correlating soil properties with rainfall all of the other soil forming agencies should remain constant. It is doubtful whether such an ideal system can be found to any great extent under natural conditions, but a few regions in the United States approach rather closely the goal set. One such region is represented by the arid-humid transition belt which extends from Colorado through Kansas to western Missouri.

CHARACTERIZATION OF THE AREA INVESTIGATED

The main soil forming factors operative in the area selected can be characterized as follows:

Moisture. The annual *precipitation* varies from 14 inches (35.6 cm.) in the semi-arid to about 38 inches (96.5 cm.) in the humid districts. For the region in question a very simple relation happens to exists between precipitation and N. S. Quotient (Meyer's ratio) which can be stated as follows:

$$\text{N.S.Q.} = 7.8R$$

where R represents annual rainfall in inches.

The normal *seasonal variation* of rainfall is consistent throughout the area and belongs to the so-called "plains type" which is characterized by dry winters and marked concentration of rainfall in the late spring and summer months.

Rainfall and N. S. Quotient do not take into consideration the water losses due to *runoff*. The relation of runoff to rainfall for the principal water-sheds of Kansas is known (5) and has the form

$$\varphi = 0.0037\ R^2 \qquad (A)]$$

[1] Contribution from the department of soils, Missouri Agricultural Experiment Station, Journal series No. 372.

[2] This agreement is remarkable indeed because the previous surface samples were collected by different persons in different localities.

where φ represents annual runoff in inches and R the annual precipitation in inches. With the aid of equation (A) the data in table 1 have been calculated and will be used in the interpretation of the soil property-rainfall curves.

Temperature. In order to keep temperature constant the soil samples were selected along an annual isotherm which has an average value of 52°F. (11.1°C.) for the states of Kansas and Missouri. The individual stations vary between 51.7°F. (10.9°C.) and 54.4°F. (12.4°C.). A few localities in Colorado report somewhat lower values, namely, 47–50°F. (8.3–10.0°C.).

Vegetation. Except for a limited number of virgin soils in Colorado and western Kansas, all samples were taken from pastures or cultivated fields. In all instances, however, the original vegetation consisted of grass. According to the map by Shantz (7) the prairie types listed in table 2 are dominant.

TABLE 1

Relation between runoff and rainfall in Kansas

	RAINFALL IN INCHES			
	10	20	30	40
Runoff in inches	0.4	1.5	3.3	5.9
Runoff in per cent of rainfall	4	7.5	11.0	14.8

TABLE 2

Nature of vegetation in the region studied

REGION	VEGETATION	APPROXIMATE RAINFALL	
		inches	*cm.*
Eastern Colorado	Grama Buffalo grass	Below 17	Below 43
Western Kansas	Wire grass	17–21	43–53
Central Kansas	Bluestem Bunch grass	21–27	53–70
Eastern Kansas and Western Missouri	Bluestem sod	27 to >38	70 to >97

According to measurements by Clements and Weaver and also on the basis of hay yields per acre the amount of organic matter produced increases regularly from west to east.

Parent Material. The entire region belongs to the great American loess belt which extends in a west-east direction over a distance of more than a thousand miles. The thickness of the smooth-surfaced loess mantle reaches in the western part in a few cases 30 to 40 feet, but mostly much less. In eastern Colorado it is perhaps more adequate to speak of wind-blown soils instead of loess, because of the coarser texture of many of the deposits. In eastern Kansas and western Missouri, the average thickness is in general much greater, and in some places near the Missouri River the loess is more than 100 feet thick. No samples were taken from the obviously young bluffs close to rivers.

In many localities, especially where the loess mantle is shallow, it is very difficult to determine the boundary between the loess and the *strata beneath.* The latter are of the following types:

Eastern Colorado and western Kansas: Tertiary deposits (Ogalolla formation) occupy all of the high plains. The materials are mainly sands in various degrees of fineness and more or less cemented by carbonate of lime. In some cases lime carbonate containing but little sand predominates.

Central Kansas: The tertiary deposits are followed by an extensive belt of the Cretaceous system, which is composed of clayey and sandy shales, chalky limestone, and sandstone, named in the order of their quantitative importance. In east central Kansas a narrow strip of the Permian system, consisting of marine shale, limestone, salt, gypsum, and sandstone, appears below the loess.

Eastern Kansas and western Missouri: The Pennsylvanian rocks composed of a series of alternating shale and limestone formations have been covered by the Kansan ice sheet. The drift deposited (now mostly covered by loess) is a heterogeneous mixture of clay, sand pebbles, and occasionally boulders. It is very much weathered and thoroughly oxidized, and the pebbles and boulders are decayed and soft. The thickness of the glacial drift is on the average not greater than 6–10 feet and in many places it is practically absent, but locally, as shown by well borings, there are accumulations of more than 60 feet.

TABLE 3

Data on topography of western Kansas

TOWN	MERIDIAN	ALTITUDE		DISTANCE		SLOPE	
		feet	*m.*	*miles*	*km.*	*feet/mile*	*m./km.*
Goodland	101° 41′	3,687	1,124	0	0		
						15.3	2.9
Colby	101° 02′	3,138	957	36	58		
						8.3	1.8
Dresden	100° 25′	2,731	832	80	129		
						13.2	2.5
Phillipsburg	99° 20′	1,939	591	140	225		
						4.6	0.9
Smith Center	98° 47′	1,800	549	170	274		
						1.0	0.2
Lebanon	98° 32′	1,812	552	182	293		

Topography. The route followed in taking the soil samples crosses the Great Plains which is an old plateau of remarkably uniform topography. In table 3 a typical section of western Kansas is listed, and it is seen that the altitude of the towns scattered over the plateau changes regularly and only slightly. Between the points selected the landscape is level or slightly undulating and occasionally rolling.

SOIL GROUPS AND CLIMATIC SOIL TYPES

The region embraces both the pedocals and the pedalfers, the boundary between the two occurring at a rainfall of about 27 inches (68.6 cm.) according

to Marbut's generalized maps (6). The isotherm followed runs through the important climatic soil types Chestnut soils, Chernozems, and Prairie soils. On the basis of Marbut's tentative maps their occurrence in Colorado, Kansas, and Missouri corresponds to the following annual rainfall data:

Chestnut soils: below 20 inches (50.8 cm.)
Chernozem soils: 20–27 inches (50.8–68.6 cm.)
Prairie soils: 27–40 inches (68.6–101.6 cm.)

Figure 1 shows the general arrangement of the major climatic soil types and the position of the 11°C. annual isotherm along which the samples were taken.

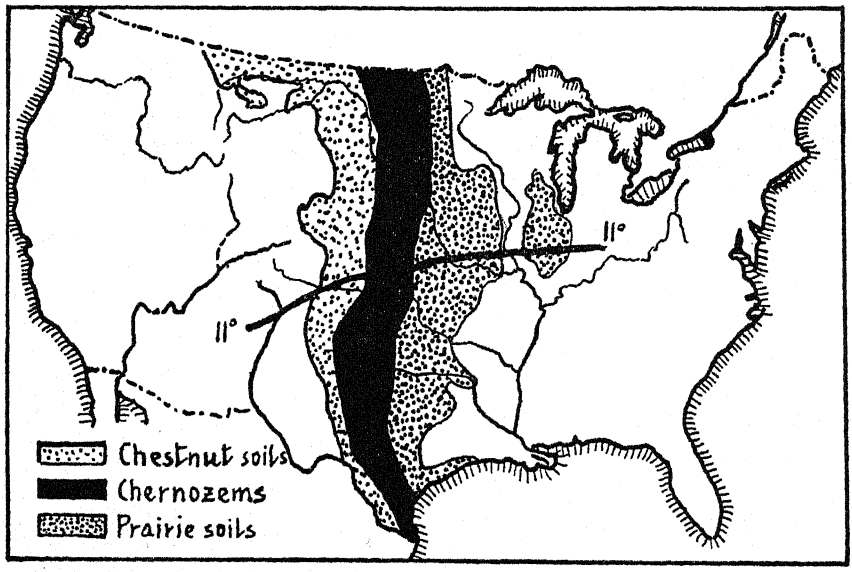


FIG. 1. CHESTNUT SOILS, CHERNOZEMS, AND PRAIRIE SOILS FORM NARROW BELTS EXTENDING FROM NORTH TO SOUTH

Note the location of the 11°C. annual isotherm along which the soil samples were collected

TECHNIQUE OF SAMPLING

In September 1931 about 100 surface samples (0–7 inches deep) were collected at intervals of 3 to 6 miles, which corresponds to about 6–10 samples per county. In addition, at least one profile was obtained from every county. In contrast to the general surface samples the profiles were collected in layers of 10-inch thickness. In the present paper mainly the data for the 10-inch surface layer are reported. The route selected often followed new highways, which permitted easy measurements of the nature and depth of the carbonate accumulation zone. The borings were taken at least 50 yards (45.7 m.) away from the road. In undulating or rolling country the highest point of the ridges was selected for sampling purposes.

ZONE OF CARBONATES

Mature soil profiles of arid and semi-arid regions possesss a zone of carbonate accumulations which recently has received considerable attention because Marbut selected it as a major criterion for soil classification. Marbut's definition: "Pedocals are fully developed profiles in which lime carbonate is found on some horizon in the solum in higher percentage than in the parent geological

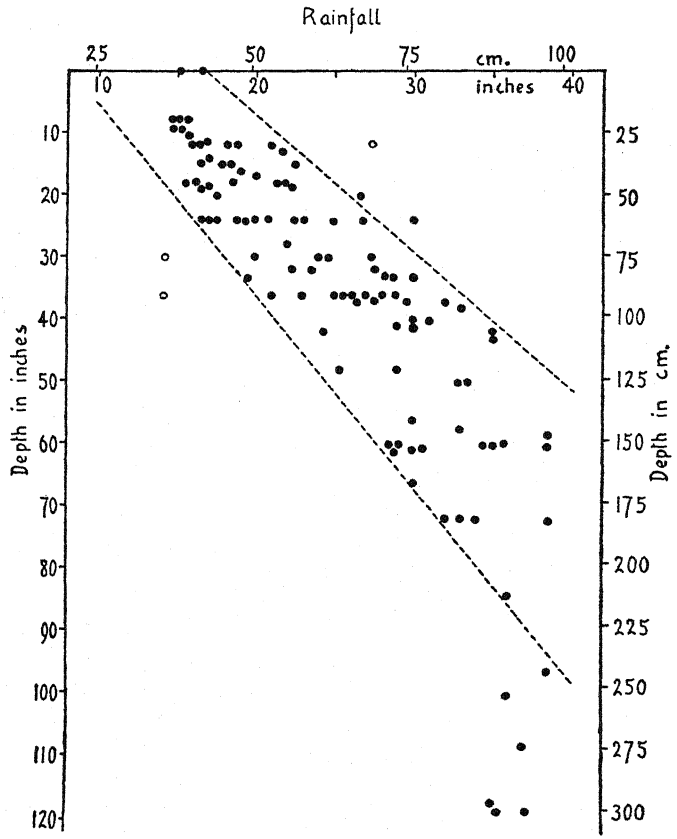


FIG. 2. DEPTH OF CARBONATE ZONE

The points indicate the position of the upper part of the accumulation zone. Observations made mainly along new highways.

formation beneath," is very clearly formulated from a logical point of view, but in the field it is frequently impossible to decide whether a lime carbonate horizon in Marbut's sense is present or not. This holds especially for soils derived from parent materials rich in carbonates.

During the entire trip the depth of the concretion zone was carefully recorded and, in case the accumulation zone was not clearly visible, the zone

nearest the surface which exhibited the strongest effervescence with dilute HCl was selected. In every case the data plotted in figure 2 refer to the depth of this upper boundary of the carbonate zone because in many soils the lime concretions are scattered throughout the entire lower part of the profile. Figure 2 very clearly shows *a linear band of considerable width which gradually descends into lower regions of the profile,* evidently as a result of leaching. The average descent begins at about 12 inches (30.5 cm.) of precipitation and proceeds at an average rate of 2.5 inches per inch of rainfall. The average depth

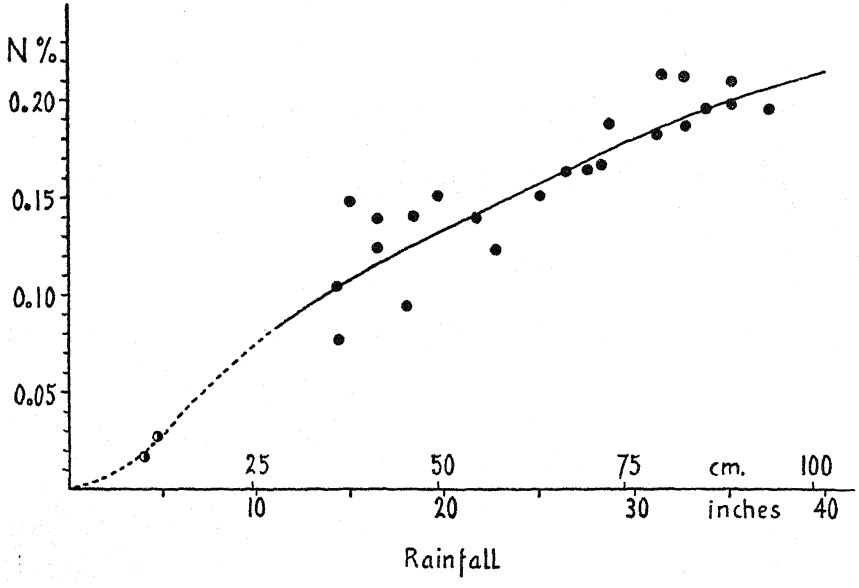


FIG. 3. NITROGEN-RAINFALL FUNCTION I

The points represent county averages (5–10 analyses) of surface soil samples 0–7 inches deep.

of this upper part of the lime horizon can be connected with rainfall (R) as follows:

$$\text{Depth} = 2.5(R-12)$$

The equation holds for R greater than 12 and smaller than 40. At lower rainfalls one would expect the curve to discontinue its linear character and approach $R = 0$.

Above 36 inches (91.4 cm.) of rainfall large lime concretions and even channels of secondary $CaCO_3$ are to be found at great depths in the highly weathered glacial till. These lime accumulations are considerably below the normal trend curve and do not necessarily represent typical lime horizons as defined by Marbut but may well be the result of ground water influences or even interglacial weathering.

NITROGEN

A nitrogen-rainfall curve along a similar isotherm has been previously published by one of the authors. The new surface samples analyzed in the present investigation confirm the earlier observations. *The nitrogen content of the soil (0–7 inches deep) as expressed by county averages varies logarithmically with increasing rainfall* as shown by the equation (fig. 3):

$$N = 0.320\ (1 - e^{-0.027R})$$

where N represents the nitrogen content of the soil in per cent and R the rainfall in inches. The constants agree very well[2] with those of the 1930 equation (3), if one takes into consideration that $H = 7.8\,R$. The scatter of the individual samples is considerable as evidenced from the correlation table 4. When a straight line relationship between nitrogen and rainfall is assumed a correlation coefficient of $+0.68$ is obtained.

TABLE 4

Classified single nitrogen analyses of surface soil samples, 0–7 inches depth

NITROGEN CONTENT OF SOIL	ANNUAL RAINFALL IN INCHES							
	0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–40
per cent								
0.20–0.25						4	2	1
0.15–0.20				12	2	14	3	3
0.10–0.15			2	20	12	6	2	
0.05–0.10			8	2				
0.00–0.05	2							

It is of interest to compare the correlation table 4 with figure 4, which gives the individual analyses of the profile samples (first horizon, 0–10 inches depth). In this case a decidedly *linear relation exists between nitrogen and rainfall* which can be represented by the equation

$$N = 0.00655R - 0.0230$$

The degree of association between the two variables is very high as indicated by the correlation coefficient, which has a value of $+0.946$. Compared with table 4 the scatter of the individual profile points about the straight line is very much less. Two reasons may account for this behavior. First, it is possible that the profiles were more carefully selected than the numerous surface samples, and secondly, the greater depth (0–10 inches) of the former as compared with 0–7 inches of the latter may be responsible for the decline in variability. Obviously the smaller the depth of sampling the greater the fluctuations of the nitrogen content between the samples.

COLLOIDAL CLAY

Though most soil scientists agree that climate may influence certain soil properties, such as pH or organic matter, it is generally considered that the texture of a soil is primarily dependent on the nature of the parent material. The results of the present investigation, however, seem to indicate that the rôle of parent material is not always so exclusive as is usually considered. All surface horizons (0–10 inches) of the profile samples were subjected to mechanical analyses, and the colloidal clay (particles smaller than 2μ diameter) was

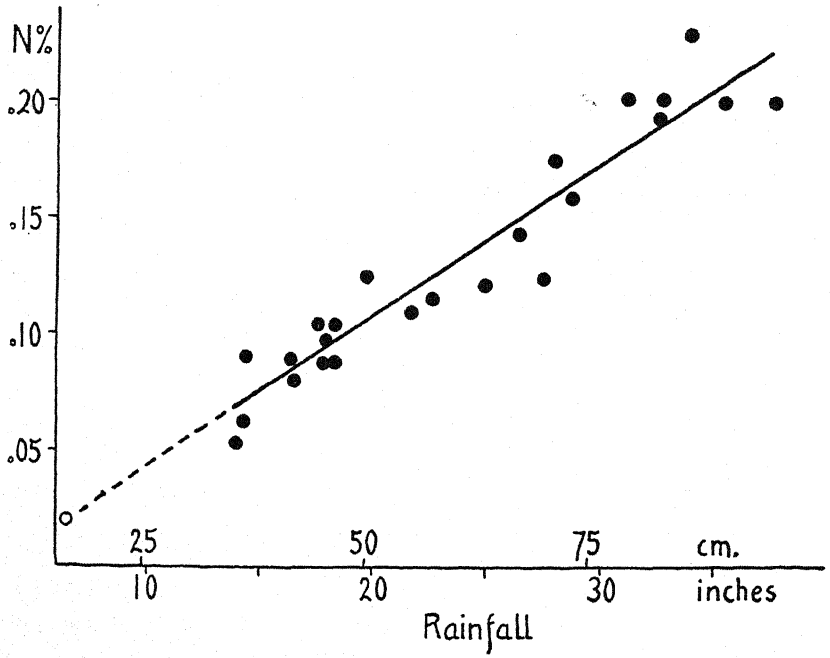


FIG. 4. NITROGEN-RAINFALL FUNCTION II

Every point refers to a single soil sample (0–10 inches surface layer) of the profile series

determined by the pipette method after oxidation of the organic matter with H_2O_2 and dispersion with sodium oxalate. From figure 5 it is clearly seen that the amount of colloidal clay in the surface soil increases regularly with increasing rainfall. The relation is very pronounced. It has a correlation coefficient of +0.820 and can be expressed by the linear equation

$$C = 0.914R + 1.33$$

where C represents the colloid content of the soil (0–10 inches) in per cent and R the annual rainfall in inches.

The observation that soil texture should be dependent on rainfall is surpris-

ing, and additional proof of such a relationship is greatly desirable. Fortunately, the numerous mechanical analyses published by the Bureau of Chemistry and Soils lend themselves to further studies.

From a similar temperature belt with a range from 52–56°F. (11.1–13.3°C.) all mechanical analyses from soil types covering more than 5 per cent of the area of a county were collected from data in the literature (1), and the clay content of the individual samples was plotted against the average rainfall of the county, as seen in figure 6. Again a decided correlation between texture

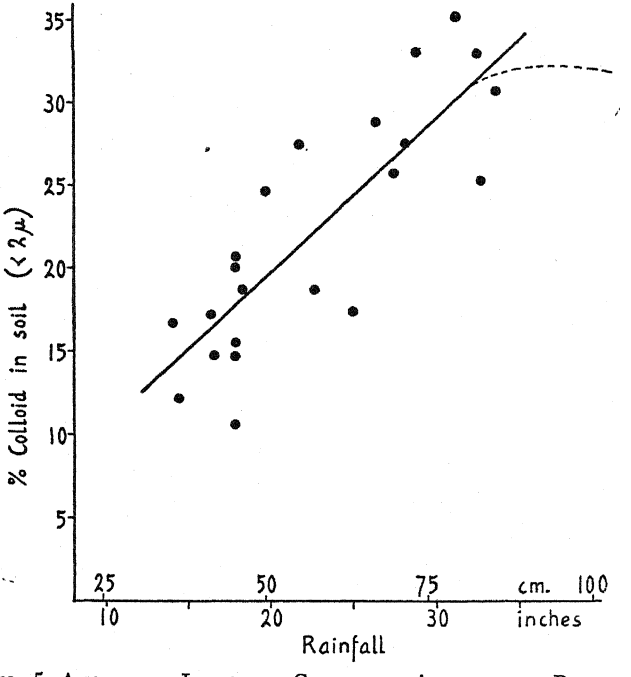


FIG. 5. AMOUNT OF INORGANIC COLLOID AS AFFECTED BY RAINFALL

(Individual samples of the profile series.) Data not included in this study indicate that under higher rainfall the colloid content of the surface soil begins to decrease as a result of eluviation.

and rainfall exists which, as measured by the correlation coefficient, has a value of +0.760. The equation fitted as usual by the method of least squares has the form

$$C_p = 0.567\ R + 4.52$$

where C_p represents the clay content of the soil in per cent and R the mean annual rainfall. *The clay curve agrees in principle with the colloid curve,* but it can not be directly compared on an absolute scale for the following reasons:

(*a*) The size of the particles determined is somewhat greater, namely "less than 5μ diameter."

(*b*) The clay determinations were carried out according to the old method of mechanical analysis using ammonia for dispersion. Compared with modern technique the amounts of clay obtained are in every case too low. However, the points in the graph are comparable among themselves.

(*c*) The clay data are not restricted to the surface layer 0–10 inches, but represent the average for the "surface soil" plus the "subsoil." The depth of sampling has not been consistent. In the majority of cases the surface soil refers to a depth of 0–8 or 0–10 inches and the subsoil extends from 8 or 10 to 36 or 40 inches. For this reason the average clay content of the "profile" was arbitrarily calculated according to the formula

$$\text{per cent clay} = \frac{S_1 + 3S_2}{4}$$

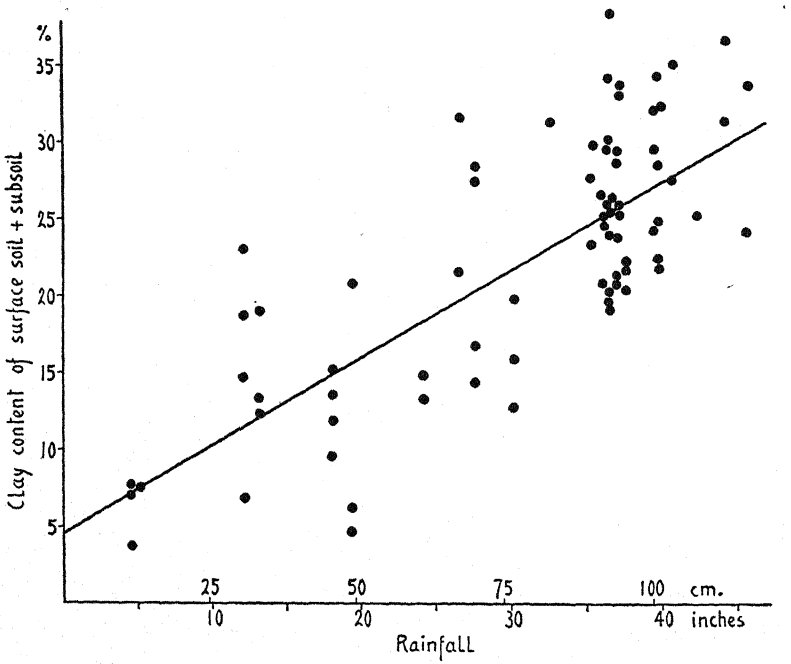


FIG. 6. CLAY-RAINFALL CORRELATION

Average clay content to a depth of 3 feet as calculated from data published by the Bureau of Chemistry and Soils.

where S_1 represents the clay content of the surface soil and S_2 that of the subsoil, both expressed in per cent.

(*d*) Parent material has not been kept constant. The soils originate not only from wind-blown material (including loess), but also from limestones, shales, sandstones, glacial till, and some tertiary lacustrine and alluvial deposits. These various types of rocks are rather evenly distributed over the entire area. The variable parent material probably is the major cause for the considerable deviations of the individual profiles from the average line.

The authors are of the opinion that the two clay equations represent not

merely a statistical association of two variables but a direct causal relationship in that the increasing moisture is considered to be responsible for the higher clay and colloid content of the soil as a result of intensified weathering.

SOIL ACIDITY

The pH determinations (quinhydrone electrode), of all surface samples have been plotted against rainfall in figure 7. The black points refer to the individual surface layers of the profile series (depth 0–10 inches), the black-white

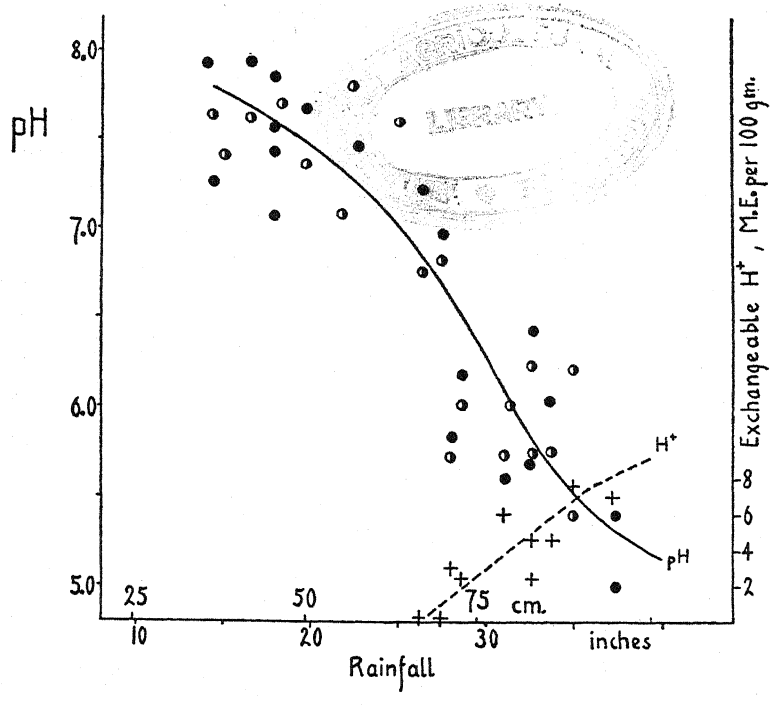


FIG. 7. SOIL ACIDITY RELATIONSHIPS. CHANGE IN pH AND EXCHANGEABLE H IONS WITH RAINFALL

Solid black points (pH) and crosses (H^+) represent the single values of the surface 0–10 inches of the profile series; black-white points refer to county averages of the 0–7 inch surface sample series.

circles represent the county averages of the numerous 0–7 inch surface samples. The resulting curve conclusively demonstrates the significance of climate as an important factor in soil formation. In the semi-arid region all soils show alkalinity, whereas acid reaction is characteristic for the humid districts. The pH extremes are linked up by a continuous series of decreasing pH values, with pH 7 (neutrality) appearing at a rainfall of about 25 inches (63.5 cm.). As a first approximation it can be said that every inch of rainfall reduces the average pH by one-tenth. The free-hand curve drawn resembles a clay titration curve of the system H-clay + $Ca(OH)_2$.

On the same graph (fig. 7) the number of exchangeable (adsorbed) H ions[3] of the profile surface layers are also shown and it is quite interesting to note that the appearance of exchange acidity coincides approximately with a soil reaction of pH 7. Both points lie in the eastern (humid) portion of the Chernozem belt. The presence of exchangeable H ions in the surface soil is typical for the semi-humid and humid regions, and the amounts are the greater the higher the rainfall.

When the saturation capacity curve in figure 8, is taken into consideration, it is evident that the pH value is directly correlated with the amounts of ex-

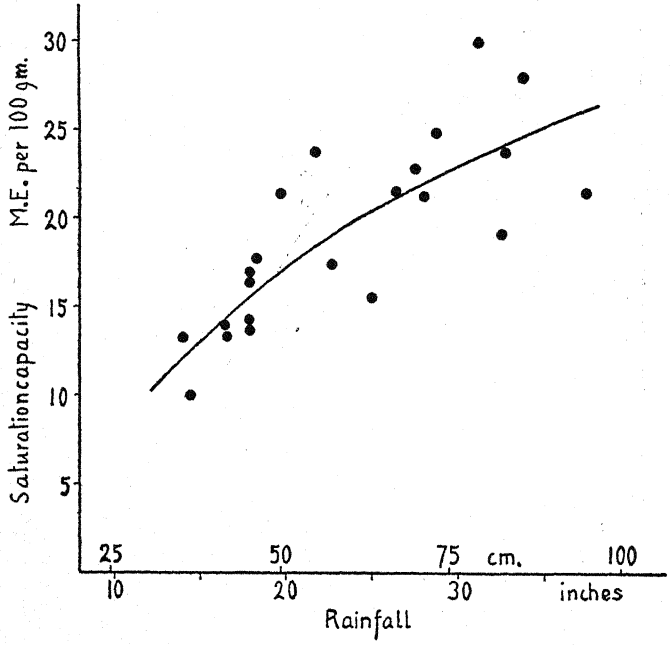


FIG. 8. SATURATION CAPACITIES OF THE 0–10 INCH SURFACE SAMPLES
Expressed by milliequivalents of total exchangeable cations per 100 gm. of soil

changeable H^+ and exchangeable bases, as far as the region below pH 7 is concerned. The descending branch of the pH curve can be fairly well described by the equation

$$\text{pH} = -0.07\,R + \log \frac{\text{exch. bases}}{\text{exch. } H^+} + 7.5, \text{ for } 26 < R < 40$$

where R represents annual rainfall and $\log \frac{\text{exch. bases}}{\text{exch. } H^+}$ refers to the base ratio which exists at any R.

[3] Determined by leaching with and subsequent electrometrical titration of originally neutral Barium acetate.

SATURATION CAPACITY

The saturation capacity or the total amount of exchangeable (adsorbed) cations including the hydrogen ions was determined by distillation with MgO of the NH_4 from the NH_4- saturated soil which had been prepared by leaching with neutral NH_4Cl and subsequent washing with alcohol. Figure 8 shows that with increasing rainfall the adsorption capacity of the soil for cations

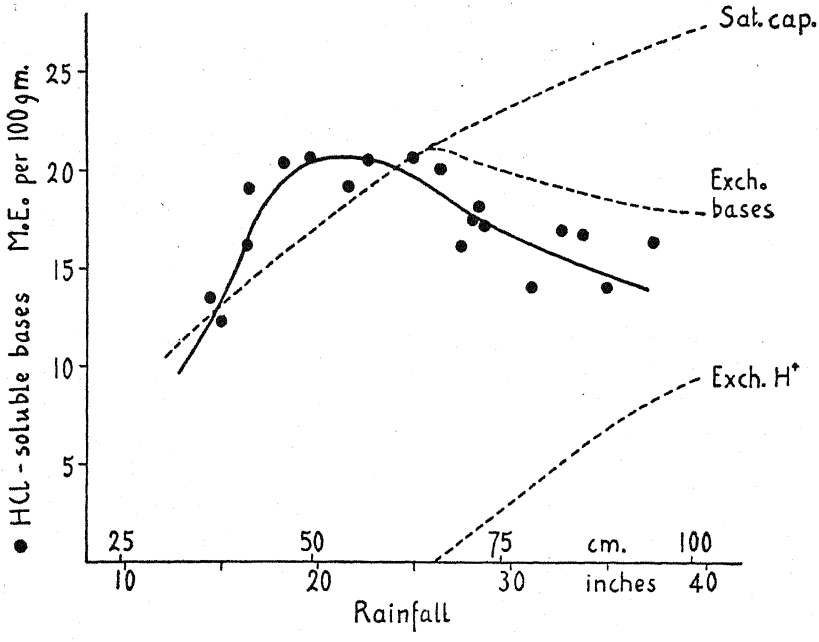


FIG. 9. RELATION BETWEEN EXCHANGEABLE CATIONS AND RAINFALL

The dotted lines refer to the 0–10 inch surface sample series, and the black points represent the total HCl-soluble bases of the 0–7 inch surface sample set assembled into county averages.

becomes gradually greater. The following equations satisfactorily describe the trend of the curve:

$$S = 32.40 \log R - 24.78 \qquad \text{for } 10<R<40$$
$$S = 14.06\, ln\, R - 24.78$$

where S represents the saturation capacity in milliequivalents per 100 gm. of soil, and R the rainfall. If R^1 is substituted for log R a straight line results which has a correlation coefficient of $+0.815$, indicating a pronounced correlation between rainfall and saturation capacity. The ascending trend of the curve in figure 8 is to be expected, since the amounts of colloidal clay and of the organic matter, which both are the seat of exchange adsorption, also become greater as rainfall increases (figs. 4 and 5).

EXCHANGEABLE CATIONS

The saturation capacity indicates how many exchangeable cations are contained in 100 gm. of soil. These were determined according to the following standard methods.

(*a*) *Exchangeable H ions:* Ten grams of soil was leached with normal neutralized Ba-acetate (pH 7) and the leachate was electrometrically titrated with $Ba(OH)_2$ to pH 7.

(*b*) *Exchangeable bases (Ca, Mg, K, Na ions):* These were determined in a lump sum by two different methods: first, by subtracting the milliequivalents of exchangeable H ions from the saturation capacity, and secondly, by a modification of the Kappen test. To 20 gm. of air-dry soil are added 100 cc. of 0.1 *N* HCl, the mixture is shaken for 1 hour, let stand for 15 hours, shaken again (a few times by hand) and after settling, the clear supernatant liquid is siphoned off and titrated in the cold with NaOH using brom thymol blue as an indicator. All data are expressed in milliequivalents per 100 gm. of soil.

In figure 9 the results are given separately for the profile surface layers (dotted lines) and the general surface samples (solid line). The latter, run by the modified Kappen test, are shown as black points which represent county averages.

From the data of the profile series it is clearly seen that in the semi-arid region the exchangeable bases are low and are equal to the saturation capacities. With increasing humidity the number of exchangeable bases becomes greater until it reaches a decided maximum at a rainfall of 26 inches. Though the saturation capacity continues to increase, the exchangeable bases steadily decrease as a result of replacement by hydrogen ions. The appearance of the latter coincides with the maximum of the exchangeable bases and is the more pronounced the more humid the climate.

The HCl-soluble bases of the general surface samples exhibit a very similar trend except that the maximum occurs at about 21 inches (52.1 cm.) of rainfall. The cause of this discrepancy probably lies in the analytical method employed and in the difference in depth of sampling.

DISCUSSION OF THE NATURE OF THE FUNCTIONS OBTAINED

The curves presented strongly suggest that soil formation is not of unconquerable complexity, and in addition they demonstrate that it is possible to isolate a major soil forming factor and describe its effect by numerical equations.

The *straight line relations* are very simple mathematical functions yet they are somewhat difficult to comprehend because they ascertain that every inch of rainfall is equally effective in the formation of a given soil property (figs. 2, 4, 5, 6). Furthermore, they lead occasionally to negative values for low moisture figures. Since it is to be doubted that rainfall effectiveness should be merely additive, one is led to conclude that the linear relationships are either coincidental as resultants of several functions, or—what is highly probable—they are restricted to relatively small areas with not too wide ranges of rainfall.

The *logarithmic curves* are more significant. They reveal that 1 inch of rain-

fall is less effective in humid regions than in arid ones. In view of the runoff data in table 1, such a behavior seems quite plausible because runoff becomes more than proportionally greater as rainfall increases. The tendency of the logarithmic curves to reach a maximum suggests that under high rainfall an additional inch of rain has little effect on soil formation.

Sigmoid curves. Though the logarithmic curves appear reasonable in describing the rate of soil formation under abundant rainfall, they can not be considered truly representative for soil conditions in arid regions. According to the slopes of the logarithmic curves the first inch of rainfall (or its equivalent in any other moisture value) should be the most effective one, a conclusion

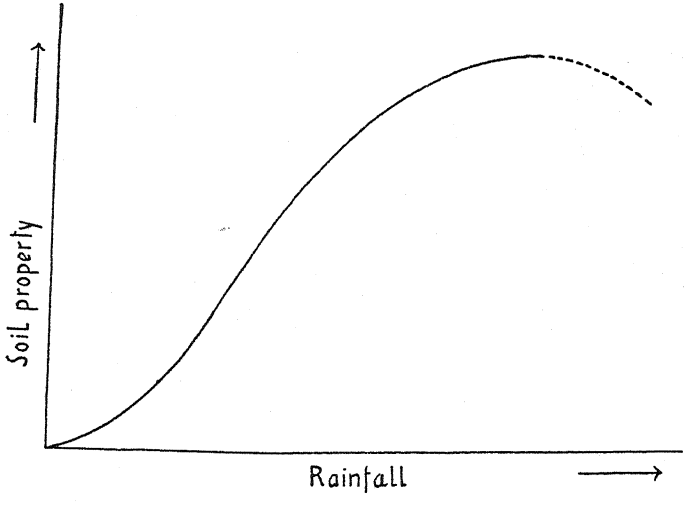


FIG. 10. GENERALIZED SIGMOID CURVE SHOWING AN INFLECTION POINT IN THE SEMI-ARID REGION AND A MAXIMUM UNDER HIGH RAINFALL

which disregards the appreciable moisture holding capacity of any parent material and soil. A sigmoid curve of the general type

$$y = \frac{a}{1 + be^{F(x)}}$$

as shown in figure 10 would be more satisfactory and would embrace a considerable number of soil property-rainfall functions. Such curves may also contain maxima, as have been found for the exchangeable bases.

INTENSITY OF SOIL FORMATION

The magnitude of the differential coefficients (slopes) of the curves permits a quantitative insight into problems of intensity of soil formation.

Rainfall effectiveness. Generally speaking the effectiveness of one inch of rainfall (R) is highest at the point where the value of $f'(R)$[4] reaches a maximum.

[4] $f'(R)$ represents the derivative of the function $f(R)$.

On the basis of sigmoid curves such as represented in figures 3 and 10, that particular point (inflection point) appears to occur in the semi-arid region. In other words, it is in dry regions with steppe-like soils that 1 inch of rainfall is most powerful in its effect on soil formation processes, such as nitrogen accumulation, development of saturation capacities, and formation of colloids. In regard to pH, however, the critical point lies in the semi-humid region.

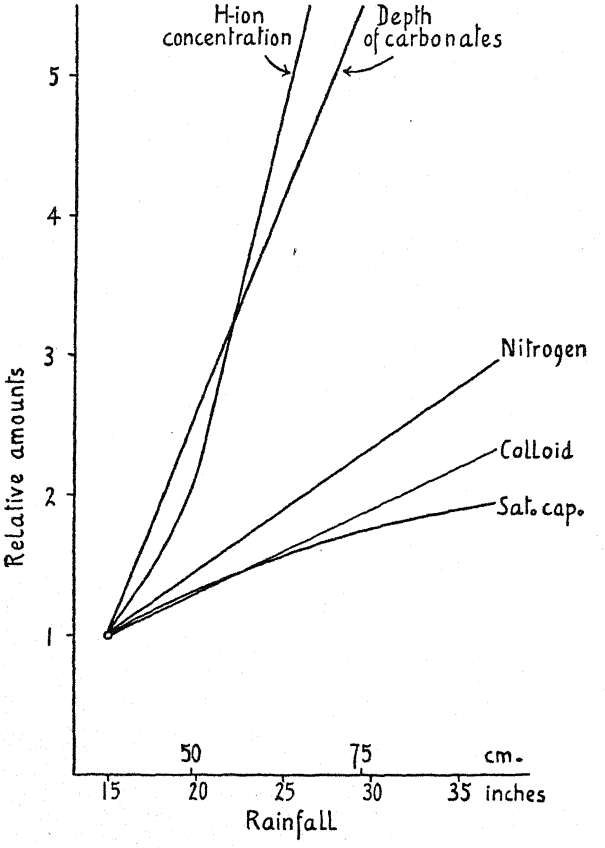


FIG. 11. RELATIVE SOIL PROPERTY-RAINFALL CURVES DEMONSTRATING THAT VARIOUS SOIL CHARACTERISTICS EXHIBIT DIFFERENT RATES OF FORMATION

Rate of soil formation, $f'(R)$. The influence of rainfall upon soil formation is not the same for all constituents involved in the process, and furthermore, it often varies with the amount of rainfall itself. This contention is well illustrated in figure 11, which shows the formation of certain soil characteristics on a comparable basis. These relative curves were obtained by arbitrarily putting the value of the soil property at $R = 15$ equal to 1. Three groups of curves can clearly be distinguished:

High rate of formation = H-ion concentration, depth of carbonate horizon.
Medium rate of formation = nitrogen (and organic matter).
Low rate of formation = colloidal clay, saturation capacity.

The magnitudes of these various rates for the rainfall interval 15–35 inches are listed in table 5, which also contains the percentage increase of the soil properties for the same moisture interval. *Evidently the H-ion concentration (negative antilog of pH) and the depth of the carbonate horizon react most sensitively toward rainfall. Next comes nitrogen and finally clay and saturation capacity.* Nitrogen increases 1.75 times, or 75 per cent, faster than colloidal clay. The crossing of the carbonate over the H-ion curve is particularly instructive. Under low rainfall, H ions increase at a slower rate than the carbonates are being translocated, whereas under high rainfall, the reverse takes place. Evidently carbonates in the soil act as a buffer toward increase in acidity, and it is not until the buffer is sufficiently removed that H ions can accumulate at full

TABLE 5

Relative intensities of soil formation for the rainfall interval 15–35 inches

(Surface layers of profiles)

SOIL PROPERTY	FUNCTION	INCREASE OF SOIL PROPERTY BETWEEN 15–35 IN.	AVERAGE RELATIVE RATE OF INCREASE (SLOPE) $f'(R)$
		per cent	
H-ion concentration		18,700	$1600 \cdot 10^{-2}$
Depth of carbonates	$D = 2.5\,(R - 12)$	667	$33.3 \cdot 10^{-2}$
Nitrogen	$N = 0.00655R - 0.023$	175	$8.7 \cdot 10^{-2}$
Colloidal clay	$C = 0.914R + 1.33$	122	$6.1 \cdot 10^{-2}$
Saturation capacity	$S = 14.06\,ln\,R - 24.78$	90	$5.0 \cdot 10^{-2}$

speed. This conclusion based on numerical functions obtained in the field agrees with what one would expect on the basis of chemical laws.

LOCATION OF BOUNDARY BETWEEN ARID AND HUMID CLIMATES

Geographers and climatologists have made considerable efforts to locate the boundary between arid and humid regions. Their attempts rest mainly on comparisons of rainfall and evaporation or discharge of rivers. For instance, Penck defines the boundary as the point at which evaporation is equal to precipitation. Often the hundredth meridian, which corresponds to a rainfall of 20 inches (50.8 cm.) for the region studied by the authors, has been taken as an approximate boundary line. The data obtained in this investigation throw some interesting light on the problem as viewed from the standpoint of soil characteristics as an index of the division line. In certain respects the climatic boundary should be related to Marbut's major soil boundary which divides all mature soils into pedocals and pedalfers on the basis of the presence or absence of a lime horizon. Marbut tentatively puts the boundary into Clay County,

Kansas, which corresponds to an annual rainfall of 27–28 inches (70 cm.). Since figure 2 discloses that in the region selected by Marbut the carbonate layers descend gradually with increasing rainfall without abrupt breaks, it is not known why the particular lime-depth 20–60 inches has been selected as the critical one. Mathematically speaking the lime horizon-rainfall relation is a monotone continuous function and as such is not well suited for classification purposes, unless it be connected with at least one other function, say the depth of the solum for example.

Of special interest are the exchangeable H ions and total exchangeable bases. At 26 inches the soils begin to contain measureable amounts of exchangeable H ions, and one might—in agreement with Gedroiz (2)—characterize the two regions by the absence or presence of exchangeable H ions. The total exchangeable bases also are significant because their rainfall function exhibits a maximum. One might set the arid-humid boundary at that locality where the

TABLE 6

Criteria and locations of the arid-humid boundary

CRITERIA	LOCATION IN KANSAS (COUNTY)	AVERAGE ANNUAL RAINFALL		ANNUAL N.S.Q.	ANNUAL TEMPERATURE
		inches	*cm.*		°C.
100th meridian	Graham	20	50.8	156	11
Marbut lime horizon	Clay	27	68.6	210	11
Neutral reaction (pH = 7)	Cloud	25	63.5	195	11
Appearance of exch. H+	Cloud	26	66.0	202	11
Max. of exch. bases	Cloud	26	66.0	202	11
Meyers value in Central Europe (discharge of rivers).....		16.5	42	207	8–10

average exchangeable bases are highest, or $f'(R) = 0$. For the pedocals $f'(R)$ would be positive, for the pedalfers it would be negative. In other words, the two major groups would be separated on the basis of the plus or minus sign of the differential coefficient. Naturally the exact geographical position of the boundary depends on the method of soil sampling and analysis, but this does not affect the definition of the criteria previously formulated (compare table 6).

SUMMARY

Along the 11°C. isotherm numerous soil samples were collected from fairly uniform parent material consisting primarily of wind-blown deposits. The variations in annual rainfall cover a range of 14–38 inches (35.6–96.5 cm.).

The zone of carbonate accumulation was found to decrease at a rate of 2.5 inches for each inch of rainfall.

Nitrogen increases continuously with increasing rainfall. The functions obtained confirm those previously published.

Under high rainfall the formation of colloidal clay is intensified. It increases at a rate of about 1 per cent per inch of rainfall.

Soil acidity changes regularly from pH 7.8 in the semi-arid region to pH 5.2 in the semi-humid one. Neutral reaction is reached at about 25 inches of rainfall (N.S.Q. = 195). Exchangeable H ions appear at 26 inches of rainfall (N.S.Q. = 202), and become very numerous in the semi-humid region.

The saturation capacity has a value of 12 m.e. per 100 gm. of soil in the semi-arid region and increases logarithmically to 27 in the semi-humid areas.

The exchangeable bases exhibit a maximum (21 m.e.) at a rainfall of 26 inches (N.S.Q. = 202).

On the basis of differential coefficients the relative rate of formation is highest for the H-ion concentration and removal of carbonates. It is lowest for the clay formation and development of saturation capacity. Nitrogen and organic matter occupy an intermediate position.

The boundary between arid and humid climates as based on the soil properties investigated appears to correspond to a rainfall of 25–26 inches (N.S.Q. 200) for the 11°C. isotherm.

REFERENCES

(1) Bureau of Chemistry and Soils, U. S. Dept. Agr., Field Operations:
1902: 593–609; 623–642; 729–776
1903: 875–889; 891–909; 911–926
1904: 791–814; 815–843; 845–858; 875–894; 895–923; 951–993
1905: 865–878; 911–926
1906: 911–941
1908: 1093–1120
1909: 1367–1399; 1477–1516
1910: 1261–1293; 1295–1316; 1345–1442
1911: 1603–1633; 1991–2058
1912: 1853–1892
1913: 1723–1756
1914: 1943–1974; 1975–2004; 2027–2055
1916: 1971–2004
1917: 1455–1482
1920: 813–837
1921: 323–348
1923: 201–245

(2) GEDROIZ, K. K. 1929 Der adsorbierende Bodenkomplex und die adsorbierten Bodenkationen als Grundlage der genetischen Bodenklassifikation. *Kolloidchem. Beihefte* 29: 149–260.

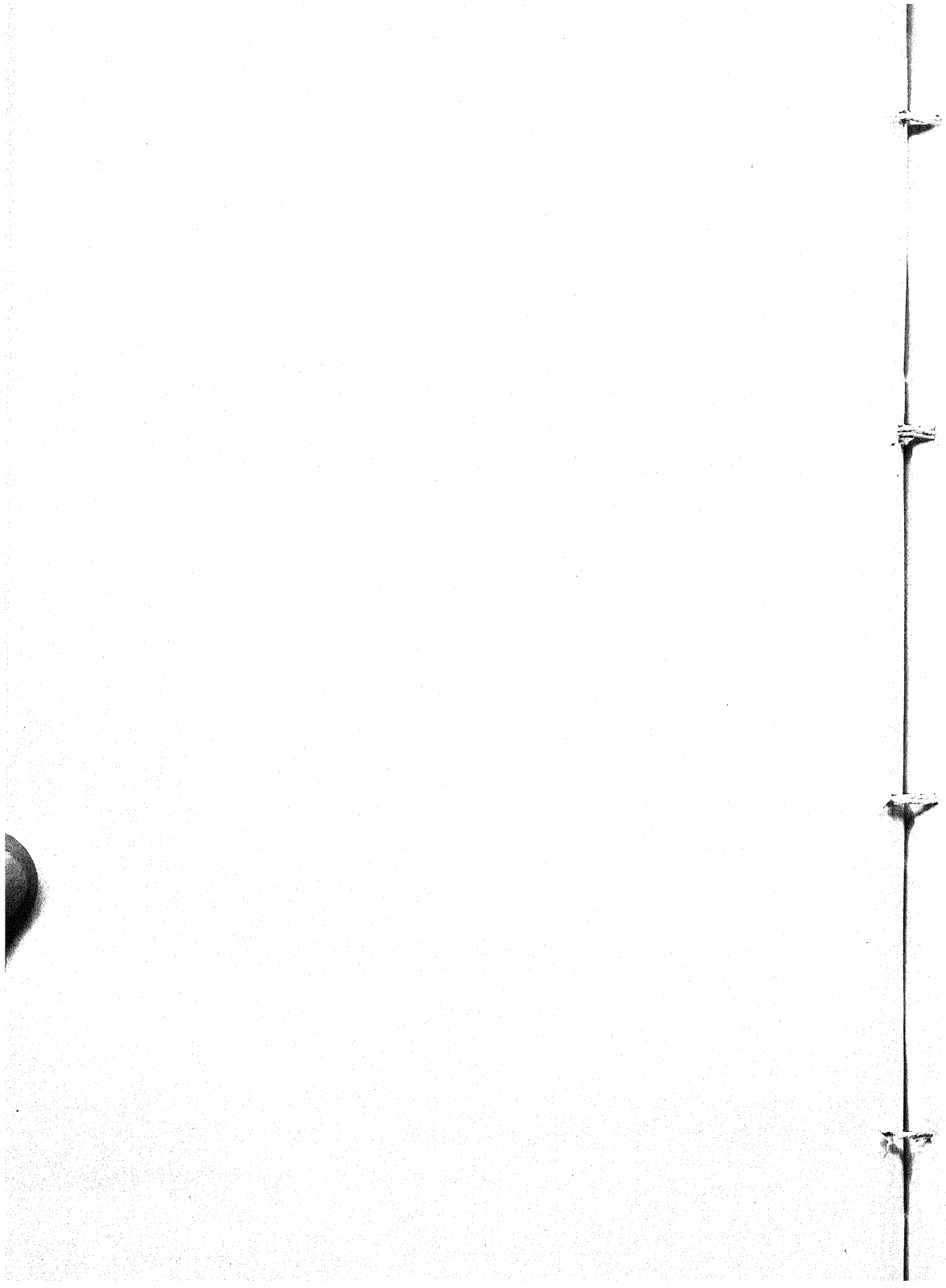
(3) JENNY, HANS 1930 The nitrogen content of the soil as related to the precipitation evaporation ratio. *Soil Sci.* 29: 193–206.

(4) JENNY, HANS 1931 Behavior of potassium and sodium during the process of soil formation. Missouri Agr. Exp. Sta. Res. Bul. 162.

(5) JUSTIN, J. D. 1914 Derivation of runoff from rainfall data. *Trans. Amer. Soc. Civil Engin.* 77: 346–384.

(6) MARBUT, C. F. 1928 A scheme for soil classification. *Proc. First Internatl. Cong. Soil Sci.* 4: 1–31.

(7) SHANTZ, H. L., AND ZON, R. 1924 Natural Vegetation. Atlas of American Agriculture. U. S. Dept. Agr. Advance Sheet 6.



SUBDIVISION OF THE UPPER PENINSULA EXPERIMENTAL FOREST[1] ON THE BASIS OF SOILS AND VEGETATION

S. A. WILDE AND H. F. SCHOLZ[2]

Lake States Forest Experiment Station

Received for publication November 13, 1933

Forest tracts are usually classified for purposes of forest management on the basis of vegetative cover type. Frequently, such a classification when considered alone is unsatisfactory, since cover type may be, and often is, a temporary condition and thus does not give a true expression of forest productivity or indicate the form of management that should be practiced. There is a need for something more basic and fundamental.

It was believed that an investigation of the genetic features of the soil would throw much light on the question. Accordingly, a study was made during 1929 of the soils and vegetation of the Upper Peninsula Experimental Forest, located at Dukes, Michigan. At this time 150 soil profiles were investigated, and the composition and growth of the forest and herbaceous vegetation were observed on a number of sample plots. From the information obtained, the area was subdivided into ecologically uniform compartments in order to establish a natural basis for all silvicultural management such as cutting, thinning, and planting. The methods and results of the study are summarized briefly in this paper.

GENERAL CHARACTERISTICS OF THE AREA

The experimental tract comprises the north half of section 35, and the south half of section 25, in Township 46 North, Range 23 West.

The climate of the area is typical of a podzol region (6). The mean annual temperature is 39°F. The highest temperature is about 96°F.; the lowest, minus 40°F. The mean annual precipitation is 33 inches. The mean temperature for the growing season (June 1 to September 30) is approximately 59°F. The precipitation for the same period is 14 inches. Approximately half of the days during the growing season are wholly or partially cloudy. The general altitude of the tract is about 400 feet above the level of Lake Superior. The topography is of a gently rolling character, and with local differences in elevation not exceeding 50 feet. The country rock of the area is Upper Cambrian sandstone. For the most part, this is covered with an unassorted drift derived from sandstone and crystalline rocks. The depth of the drift sheet is

[1] Field station of Lake States Forest Experiment Station.

[2] Formerly field assistant and junior forester, respectively.

in places as shallow as 2 feet, but is ordinarily deeper. In a few localities, between the sandstone and the till, is found a layer of highly calcareous lacustrine clay. Some of the morainic depressions are filled with the remains of aquatic and swamp vegetation. The narrow bands along the creeks include recent post-glacial deposits of mineral and organic matter. The surface of the area is drained by the headwaters of Whitefish River and several creeks. The internal drainage of the soil is often poor as a result of the influence of near-surface sandstone, or colloidal glacial till.

Twelve tree species—six deciduous and six coniferous—are found in the virgin forest of the Dukes' area. They are: sugar maple (*Acer saccharum*, Marshall), yellow birch (*Betula lutea*, Michaux), basswood (*Tilia glabra*, Ventenat), American elm (*Ulmus americana*, L.), red maple (*Acer rubrum*, L.), black ash (*Fraxinus nigra*, Marshall), eastern hemlock (*Tsuga canadensis*, L., Carriere), white spruce (*Picea glauca*, Moench, Voss), balsam fir (*Abies balsamea*, L. Miller), tamarack (*Larix laricina*, DuRoi, Koch), black spruce (*Picea mariana*, Miller, Briton), and northern white cedar (*Thuya occidentalis*, L.) Among the more important woody plants are: leatherwood (*Dirca palustris*), ground hemlock (*Taxus canadensis*), tag alder (*Alnus rhombifolia*, Nuttal), and dogwood (*Cornus florida*).

METHOD OF STUDYING AND SUBDIVIDING THE FOREST

In a preliminary survey, a rough contour map was prepared, and the natural elements of topography, such as hill tops, elevated shelves or flats, basins, and valleys, were blocked out. After the area had been subdivided upon the basis of its topographical features, soil profiles were dug. The thickness of each layer, its physical and chemical character, the depth to which roots penetrated, conditions of moisture, and the depth at which the water table occurred were recorded both descriptively and graphically (fig. 1). In addition to this a complete set of soil samples and 10 monoliths of representative soil profiles were taken and carefully investigated.

Different layers or horizons of the profile were designated according to Glinka (1), as follows: A_0—forest litter; A_1—infiltrated or humic layer; A_2—eluvial, leached, or podzolic horizon; B—illuvial or accumulative horizon; C—parent material of the soil (rock or weathered substratum); G—deoxidized or gley horizon, formed by the action of ground water. The forest floor has been classified after Mueller (4) and Hesselman (2) into two major types: *mull* and *raw humus*. The standard United States textural classification, viz., sand, sandy loam, fine sandy loam, silt loam, and clay, has been used in the description of the soil profiles (5).

With a few exceptions, the parent soil material of the entire area is stony and gravelly fine sandy loam. In spite of this textural homogeneity of the soil, the forest vegetation shows essential differences in its composition and growth. It was found that these differences have resulted largely from the so-called genetic, or clima-zonal features of the soil, such as leaching, development of

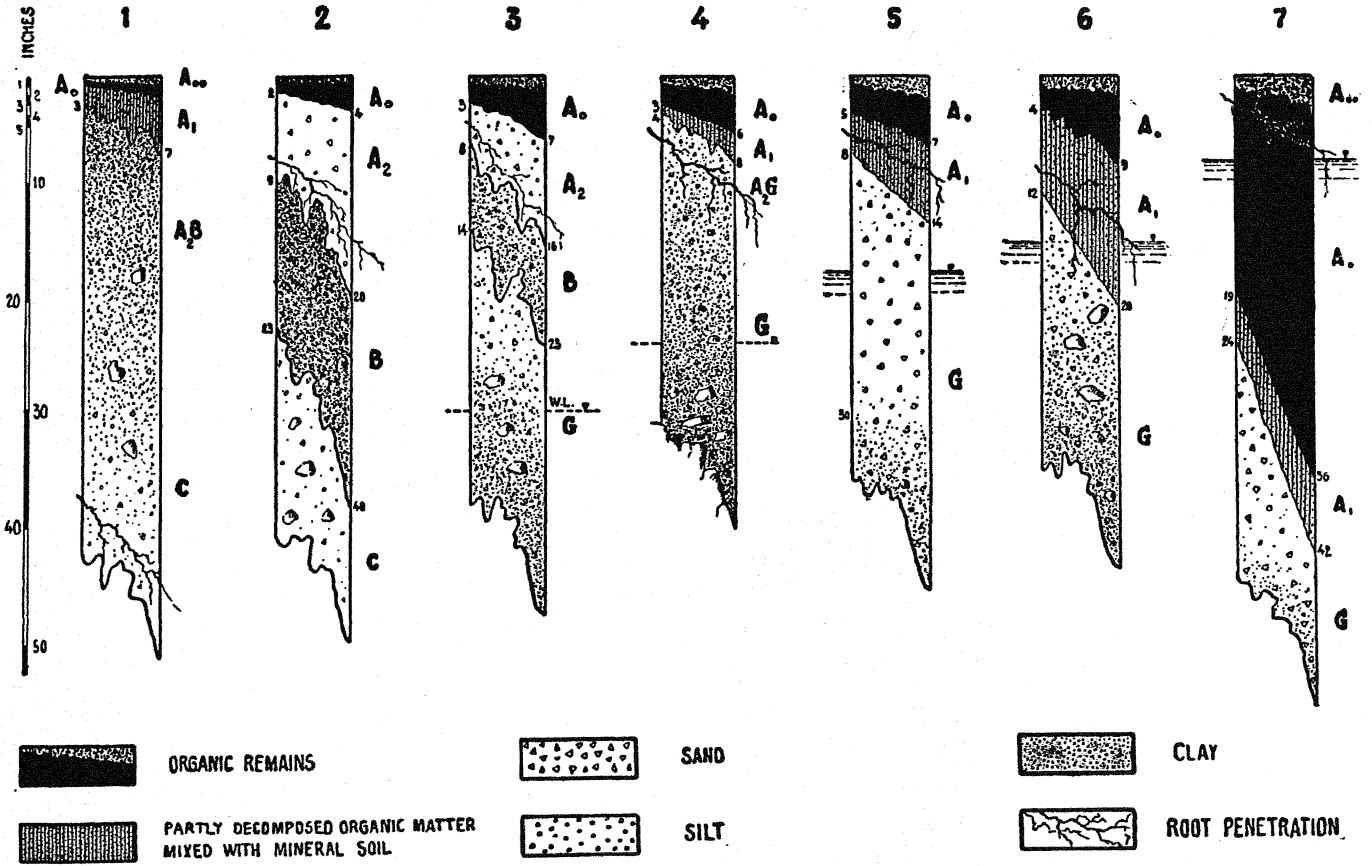


FIG. 1. SCHEMATIC REPRESENTATION OF TYPICAL SOIL PROFILES, SHOWING THE MINIMUM AND MAXIMUM DEPTHS OF THE HORIZONS

1. Slightly podzolized loam; 2, loamy podzol with hardpan; 3, swampy podzol with hardpan and gley, formed on glacial till; 4, swampy podzol with gley, formed on sandstone; 5, formed on alluvial sand; 6, muck, formed on glacial till; 7, woody peat.

cemented hardpan layers, reduction of chemical compounds, hydrolysis, formation of sticky and mottled strata, and accumulation of undecomposed organic matter (3, 9).

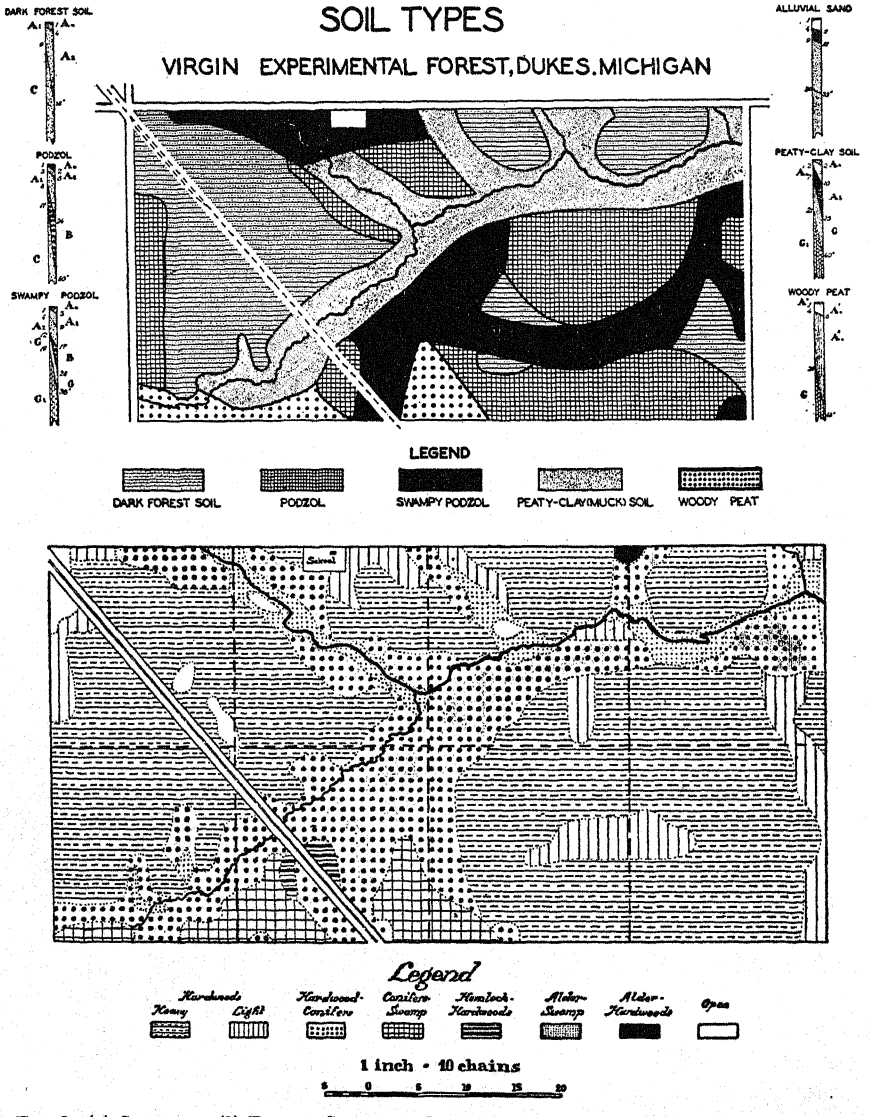


FIG. 2. (*a*) SOILS AND (*b*) FOREST COVER OF VIRGIN PORTION OF THE EXPERIMENTAL FOREST
Section 35, Township 46, North, Range 23, West

In the light of these facts, a strictly genetic classification of the soil was adopted for mapping the soils, and five soil types were recognized, as follows: (*a*) slightly leached, or slightly podzolized loam, or "dark forest soil"; (*b*)

strongly leached and cemented soil, or "podzol"; (*c*) poorly drained, leached and mottled soil, or "swampy podzol"; (*d*) half organic, half mineral soil, in areas subject to overflow, or "muck"; (*e*) organic deposits, or "woody peat."

On the basis of these soil types, the area was subdivided into compartments. The boundaries of these compartments were laid out with a compass and chain, the trees along them were blazed, and a soil map was prepared (fig. 2a). Independently of the soil work, a forest cover map (fig. 2b) was made by E. L. Mowat, who was in charge of the Upper Peninsula Forest during 1929.

SOILS, FOREST COVER, AND HERBACEOUS VEGETATION

Slightly podzolized soils (dark forest loam, mull loam)

The slightly podzolized type of soils occupies the higher, well-drained areas such as elevated benches and slopes. The soil is of a fine sandy loam texture, nearly uniform throughout the profile, and is characterized by a dark grayish brown color. The top layer shows a complete mineralization of organic remains, and an abundance of readily available mineral plant food. The mineral soil has a loose, somewhat crummy structure, adequate water-holding capacity, and perfect aeration. Acidity varies fron pH 5.5 to 6.5. The roots penetrate to a depth of 4 to 5 feet, or more. Ground water seldom occurs at a depth of less than 10 feet. The description of a typical profile follows (plate 1a):

- A_0' Thickness 0.5 to 1.0 inch. Undecomposed maple leaf litter.
- A_0'' Thickness about 1.0 inch. Half decomposed mull mulch of a dark brown color and granular structure. Interwoven with roots. Slightly acid or nearly neutral. Has the odor of good garden soil.
- A_1 Thickness 1.0 to 2.0 inches. Dark gray humic layer of a loamy texture, infiltrated with the products of mulch decomposition. Slightly acid.
- A_2 Not present, or appears as small grayish spots in the upper portion of the profile.
- B Not present.
- C Thickness about 35.0 inches. Dark brownish gray fine sandy loam, mixed with gravel and some larger fragments of sandstone and granitic rocks. Moderately acid in reaction (pH 5.5). At a depth of 3 to 4 feet it grades into an unassorted glacial till underlain by a somewhat fractured plane of sandstone.

Slightly podzolized soils are associated with a pure hardwood type consisting of sugar maple, basswood, American elm, and some yellow birch. The understory of stands consists of a luxuriant reproduction of sugar maple, partially of seed and partially of sprout origin (plate 2a). With the exception of leatherwood, few shrubs are present. Ground cover vegetation is limited to Solomon's seal (*Polygonatum biflorum*), false Solomon's seal (*Smilacina racemosa*), twisted-stalk (*Streptopus roseus*), bellwort (*Uvularia perfoliata*), and some species of Viola. The scarcity both in species and number of herbaceous flora is one of the striking features in these virgin hardwood stands. Floristically, therefore, these areas may be classified as the *Acer-Nudum* type (plate 2a).

Podzol soils (strongly leached and cemented loam)

The podzol soil occurs on knolls, ridges, and elevated flats. The texture is often slightly sandier than that of the mull loam just described. The organic

matter is accumulated as raw humus. Relatively strong organic acids, formed as by-products of decomposition, have caused the leaching of calcium, magnesium, potassium, iron, and aluminum from the upper soil layers. In the lower part of the profile, the iron and aluminum compounds come in contact with the bases of the parent material and are precipitated. As a result of this process, the soil shows two characteristic layers: the ash-like, purely silicious, podzolic layer, and the rusty, reddish brown, ortsand or ortstein layer. Because of the translocation of chemical compounds, a considerable portion of the mineral plant foods are in a condition unavailable to plants. The reaction of the soil is extremely acid—often as low as pH 4.0, and seldom higher than pH 5.0. The soil is compacted, structureless, and as a rule cemented in the lower part of the profile. Because of the highly colloidal nature of the subsoil, the water-holding capacity is high, and aeration is not adequate for the best tree growth. Tree roots are concentrated in the upper portion of the profile. The following description is typical of the podzol soil of the Dukes' area (plate 2b):

A_0 Thickness 3 to 4 inches. Slightly decomposed organic layer of a dark brown color. Penetrated by the mycelium of fungi. Has a disagreeable sour odor, and a strongly acid reaction (pH 4.0 to 4.5). Line of demarkation between A_0 and A_2 is sharply defined.

A_1 Not present.

A_2 Thickness 9 to 12 inches. Light gray, ash-like, structureless, leached fine sandy loam. Strongly acid (pH 3.8 to 4.0). This horizon often has irregular, tongue-like lower limits.

B_1 Thickness 7 to 12 inches. Slightly cemented fine sandy loam of a coffee-brown, somewhat reddish color.

B_2 Thickness 15 to 20 inches. Rock-like, firmly cemented hardpan layer (Ortstein) of a dark coffee-brown color. Strongly acid. Free of tree roots.

C Unassorted, gravelly till.

All podzol profiles studied on the experimental area are fully developed and nearly always have a firmly cemented hardpan layer.

The forest cover on podzols is made up of hemlock, yellow birch, and somewhat inferior sugar maple. Occasionally balsam fir is present in the understory. Ground hemlock is one of the most characteristic woody plants. The herbaceous association is of a saprophilous nature, and includes the following species: Clintonia (*Clintonia borealis*), dwarf Solomon's seal (*Maianthemum canadense*, Desf.), gold thread (*Coptis trifolia*, L.), bunchberry (*Cornus canadensis*, L.), star flower (*Trientalis americana*, Purs.), wood sorrel (*Oxalis acetosella*, L.), partridge berry (*Mitchella repens*), and a number of species of club mosses (*Lycopodium lucidulum*, *Lycopodium annotinum*, *Lycopodium obscurum*, etc.). Clintonia and club mosses seem to be the best indicators of a pronounced soil degradation, and for this reason this site may be classified as the *Clintonia-Lycopodium* type (plate 2b).

Swampy podzol (mottled loam, gley soil)

The swampy podzol soil type is confined to the lower, swamp-border slopes, valleys, and basins, in areas characterized by a high water table. Because of

the surface deposition of eroded material from the upper slopes, the texture of swampy podzol is somewhat heavier than that of upland soils. The decomposition of organic remains is very slow, and some peaty material is formed. The soil is leached, compacted, and sometimes cemented. The illuvial layer grades into sticky gley horizons with reddish brown or green mottlings of ferric and ferrous iron oxides. Because of the impervious nature of the gley layer, the ground water may be within 4 to 5 feet of the surface during most of the growing season. Since the soil is excessively saturated, aeration is at a minimum. The top-soil is strongly acid, but the deeper subsoil is sometimes rendered neutral by the hydrolytic action of the water. The mineral plant food is largely unavailable to trees. Root concentration is limited to the upper soil layers. The characteristic features of a typical profile are:

A_0 Thickness 4 to 5 inches. Half decomposed dark brown or blackish brown organic accumulation. Somewhat peaty. Strongly acid.

A_1 Thickness 2 to 4 inches. Dark gray to grayish black humic loam.

A_2 Thickness 4 to 8 inches. Light yellowish gray, leached and strongly acid loam, or fine sandy loam with some fine featherings of humus compounds.

B Thickness 10 to 16 inches. Reddish brown, somewhat cemented and compacted fine sandy loam with intensively colored flakes and concretions. Acid in reaction.

G Thickness 12 inches. Yellowish gray sandy loam with an irregular admixture of clay particles. Mottled reddish brown. Sticky and plastic. Some gravel, boulders, and fragments of sandstone are present. Slightly acid. Permanently wet in the lower part of the profile.

C Sandstone bedrock.

Occurring as a transitional form between well-drained upland areas and swamps, swampy podzol shows a number of morphological variations, dependent upon the development of podzolic, ortstein, and gley layers (plate 1, c and d). All of these variations, however, have a minor ecological significance, because of the pronounced essential features: excessive moisture, insufficient aeration, and unavailability of plant nutrients.

The forest cover on swampy podzol is made up of very inferior sugar maple, red maple, mountain maple (*Acer spicatum*, LaMarck), yellow birch, American elm, black ash, and some balsam fir, white spruce, and other conifers. The percentage of these species varies considerably. Growth is poor, especially in the proximity of swamps. Shrubs and herbaceous plants include the members of both upland and swamp flora. In many places the ferns replace other species so completely that a *fern* type can be recognized (plate 2c).

Muck (peaty-clay soil, Sapropel soil)

Muck soils are confined to the low, poorly drained areas subject to overflow. As a rule, muck areas are broken by island-like formations of swampy podzol or woody peat, resulting from small changes in relief and drainage. The top-soil of muck is formed partially by the decomposition of plants *in situ*, and partially by the deposition of both mineral (silt and clay) and organic matter during inundations. The amount of inorganic particles in the upper, so-called

"Sapropel" (7) layer of soil varies from 30 to 70 per cent, and the total thickness of the layer varies from several inches to 2 or 3 feet. The substratum of muck is either unassorted till or alluvial sand (plate 1 e and f). In one case muck was found resting upon calcareous lacustrine clay which, in a dry state, reacted violently with hydrochloric acid. Muck contains a large quantity of both nitrogen and basic material (mainly calcium), and is potentially the richest of all organic soils in the region. However, because of the excessive saturation of the soil and insufficient aeration, the mineral plant food of muck is largely unavailable to the trees. A typical muck profile shows the following characteristics (plate 1e):

A_0 Thickness 3 to 5 inches. Half decomposed, dark brown organic matter of somewhat granular structure.

A_1 Thickness 15 to 18 inches. Plastic and moist brownish gray, steel or bluish gray mixture of organic, peat-like material and clay. Slightly acid (pH 6.0).

G Thickness 20 inches. Wet, compacted gravelly sandy loam of yellowish gray color with sharply pronounced brownish and greenish mottlings and agglutinations. Neutral or slightly alkaline in reaction (pH 7.0 to 7.5).

The typical forest cover on muck is comprised of water-loving hardwoods and conifers. These include red maple, black ash, yellow birch, American elm, balsam fir, spruces, tamarack, and some northern cedar. Sugar maple occurs along the upland border. Approximately 50 per cent of the trees on this type are deciduous and 50 per cent coniferous species. Tag alder (*Alnus rhombifolia*), willow (*Salix spp.*), gooseberry (*Ribes spp.*), currant (*Ribes americanum*), dogwood (*Cornus florida*), hazelnut (*Corylus colurna*), and dwarf rubus (*Rubus triflorus*) are the most common woody plants. In places, the hardwood-coniferous type is replaced by a dense growth of tag alder. The herbaceous cover is characterized by wood nettle (*Urtica Lyallii*), bed straw (*Gallium asprellum*), horse-tail (*Equisetum*), tear thumb (*Persecara spp.*), arrow head (*Sagittaria spp.*), geranium (*Pelargonium*), ferns, some mosses, and numerous grasses and sedges. Floristically this site may be classified as *Urtica-Gallium* type.

Woody peat

Woody peat is confined to the areas with somewhat stagnant water. The upper portion of the profile consists of an accumulation of slightly decomposed remains of herbaceous and tree vegetation, particularly the wood of white cedar. The underlying mineral substratum is permanently saturated with water and usually shows a typical mottling of the gley layers. The organic layers are strongly acid. The mineral subsoil is often alkaline, because of the presence of carbonates or a high saturation of base exchange material. For the most part the roots of trees and other vegetation are confined to the upper 1-foot layer. A typical woody peat profile follows (plate 1g):

A_0' Thickness 3 inches. Half decomposed leaves, needles, mosses, and roots of trees and herbaceous vegetation. Strongly acid.

A_0'' Thickness about 36 inches. Little decomposed remains of swamp trees, mainly white cedar, colored brown or black. Many fragments of wood retained their identity. These wood fragments often are slimy to the touch and have a strong, disagreeable smell of hydrogen sulfide. Strongly acid.

A_1 Thickness 3 to 8 inches. Plastic, wet, peaty-clay material of a black color, formed partly by previous decomposition of organic matter, and partly by the dispersion of mineral and organic exchange material through the agency of water.

G Wet sand with some gravel and varying amounts of clay. Green mottlings or agglutinations are common. Alkaline.

The forest cover on woody peat is chiefly northern white cedar, although a little balsam fir, white and black spruce, tamarack, black ash, and red maple also commonly occur. Most of the tamarack has been killed by the larch sawfly (*Nematus Ericksonii*), and only new growths of this tree are found at present. Some water-loving shrubs occur in limited numbers. Tag alder is found along the borders of most woody peat swamps. The principal species of ground-cover vegetation are wood sorrel (*Oxalis acetosella*), dwarf Solomon's seal (*Maianthemum canadense*), gold thread (*Coptis trifolia*), clintonia (*Clintonia borealis*), and dwarf rubus (*Rubus spp.*). Of slightly less importance are bunchberry (*Cornus canadensis*), creeping snowberry (*Chiogenes hispidula*), twinflower (*Borealis americana*), bishop's cap (*Mitella nuda*), star flower (*Trientalis americana*), some ferns, and *Polytrichum*, *Sphagnum*, *Mnium*, and other genera of mosses. Floristically this site may be classified as *Oxalis* type (plate 2d).

CORRELATION OF SOILS WITH FOREST GROWTH

Observations made in virgin stands on the Dukes area and nearby indicate that sugar maple attains somewhat greater height on slightly podzolized soil than on podzol. The height growth of this species on both of these soils is considerably greater than on swampy podzol and muck. The total number of trees per acre, the average basal area, and the average number of trees 1 to 3 inches in diameter are all greater on slightly podzolized soil than on podzol and swampy podzol soils (table 1 and 2).

The average volume per care of all-aged virgin hardwood stands (trees 100 to 300 years old) on slightly podzolized soil sometimes is as great as 12,000 board feet. The volume of hardwood stands on podzol is somewhat less. The hardwoods on swampy podzol produce 8,000; the coniferous-hardwood type on muck, 6,500; and the cedar stands on woody peat, only 4,000 board feet per acre.

It is, of course, not known whether these growth advantages in favor of the slightly podzolized loam will be maintained after the virgin stand has been treated silviculturally, but it is reasonable to expect that they will be.

SOILS AND FOREST MANAGEMENT

The soils discussed are adapted to different tree species, and show different actual and potential productivity; therefore, they require different types of forest management.

Slightly podzolized soils possess adequate moisture, perfect aeration, and an abundance of mineral plant food, and are well suited to forestry of a purely commercial character. Such soils will produce excellent stands of hardwoods. They are even better adapted to a mixture of hardwoods and conifers. The hardwoods tend to reproduce themselves no matter what system of cutting is used, but the valuable conifers must be introduced artificially if they are to

TABLE 1

Average height for sugar maple growing on slightly podzolized, podzol, and swampy podzol soils

DIAMETER BREAST HIGH	AVERAGE HEIGHT OF DOMINANT TREES ON SOILS INDICATED*					
	A	B	C	D	E	F
inches	*feet*	*feet*	*feet*	*feet*	*feet*	*feet*
10	75	65	58	66	67	72
12	79	71	62	72	73	78
14	84	75	65	76	78	82
16	88	79	69	80	82	87
18	91	82	72	83	85	90
20	94	85	74	86	88	93
22	96	87	75	89	90	96
24	98	89	..	91	93	99
26	100	91	..	93	95	101
28	102	93	..	..	97	104
30	103	95	..	..	..	106
32	104	96	..	..	..	108

* A. Slightly podzolized soil—Dukes, Michigan. Basis for values, 95 trees; average height 92 feet; standard error 4.5 feet; standard deviation 8.5 feet; alienation index 0.53; correlation index 0.85.

B. Podzol—Dukes, Michigan. Basis for values, 82 trees; average height 85 feet; standard error 6.3 feet; standard deviation 9.6 feet; alienation index 0.66; correlation index 0.75.

C. Swampy podzol—Dukes, Michigan. Mixed hardwood-coniferous forest type. Basis for values, 16 trees; average height 69 feet; standard error 4.1 feet; standard deviation 6.5 feet; alienation index 0.63; correlation index 0.78.

D. Swampy podzol—Dukes, Michigan. Ground cover principally ostrich fern. Basis for values 22 trees; average height 80 feet; standard error 4.5 feet; standard deviation 9.5 feet; alienation index 0.47; correlation index 0.88.

E. Podzol—Skandia, Michigan. Basis for values 20 trees; average height 83 feet; standard error 4.4 feet; standard deviation 9.7 feet; alienation index 0.45; correlation index 0.89.

F. Podzol without hardpan—Au Train Lake, Alger County, Michigan. Basis for values 32 trees; average height 91 feet; standard error 7.6 feet; standard deviation 12.5 feet; alienation index 0.61; correlation index 0.79.

make up any appreciable part of the new stand. A clear cutting of the old stand and immediate reforestation with valuable conifers (Norway spruce, white spruce, and white pine) accomplish this end. Such a method, however, would make a second cut impossible for a great many years to come, and would be objectionable if sustained production is desired. A gradual selective cutting and underplanting in the openings should accomplish both

purposes. The first selective cuttings should open up the stand as little as possible in order to discourage the growth of sprouts, and preserve the present ideal conditions of soil and humus. In either case, the forest would be converted into mixed stands of planted conifers and naturally reproduced hardwoods.

Podzol soils are characterized by slow humification, and a deficit of mineral nutrients. Because of the impervious nature of the subsoil, the upper layer of podzol remains wet and cool in spring. This may shorten the growing season to a slight degree. During the hot season of summer, the highly colloidal illuvial layer breaks the movement of capillary water, and vegetation often

TABLE 2

Total basal area per acre for stands growing upon different soil types

KIND OF SOIL	ENTIRE STAND DIAMETER 1–35 INCHES B.H.		ADVANCED REPRODUCTION DIAMETER 1–3 INCHES B.H.	
	Total trees	Basal area	Total trees	Basal area
		sq. ft.		*sq. ft.*
Slightly podzolized soil	940	220	750	9.4
Slightly podzolized soil	768	197	640	6.4
Slightly podzolized soil	820	198	644	8.8
Average*	870	209	700	8.5
Podzol	398	140	264	3.6
Podzol	636	125	494	3.9
Podzol	715	153	575	7.9
Average†	557	135	418	4.4

* Weighted average based on 75, 1/50-acre plots. Approximately 95 per cent of total trees per acre are sugar maple.

† Weighted average based on 65, 1/50-acre plots. Approximately 82 per cent of total trees per acre are sugar maple.

suffers from drought. These features become especially pronounced after clear cutting. For this reason selective cutting is the better method of forest management on these soils. From the standpoint of soil improvement, a pure hardwood stand with a predominance of sugar maple is here the best type of forest cover. Yellow birch should also be encouraged, since it is one of the more valuable trees of the hardwood type. In order to hasten the decomposition of raw humus, fairly heavy partial cuttings should be made. However, along the boundaries of stands and at other places where the timber is exposed to strong winds, logging should be limited to defective or over-mature trees. Particularly is this true of stands on podzol with a hardpan layer, for here the

root systems are very superficial and the trees are especially subject to windthrow.

Swampy podzol soils are not well suited to the production of hardwoods. This is particularly true with respect to sugar maple, for on swampy podzol this species grows slowly, has poorly-shaped stems, and shows a high percentage of cull. The reason for this lies chiefly in the insufficient aeration of the soil. Under such conditions, the hardwood species, excepting yellow birch, should be replaced gradually by the conifers, which are better able to stand soil stagnation. White spruce, Norway spruce (*Picea excelsa*), and balsam fir are the most valuable commercial species adapted to this soil. The conversion of the forest can be accomplished through a thinning and an underplanting. Because of the danger from early and late frosts and "heaving," the mound method of planting will have a great advantage on this site. There is apt to be less heaving in spring planting.

Muck soils usually support stands of little commercial value. Nevertheless, from the standpoint of conservation, the preservation and the improvement of the forest cover on these soils are essential. The mixed hardwood-coniferous stands in the alluvial valleys, with their accompanying dense growth of shrubs and grasses, and running water furnish an ideal refuge for game. For this reason, when a selective cutting or thinning is made, the secondary trees and shrubs which supply food for birds and animals should be protected. Available firewood, pulpwood, and conifers for christmas trees should be cut during the winter months. This disturbs the game less, and is the most practical time to log wet ground.

Woody peat ordinarily supports only one species of commercial value—northern white cedar. This may be cut wherever it is available. The only silvicultural requirement is to leave enough healthy, mature trees over the area to secure natural reproduction. If stands of this type contain some balsam fir and spruce, these species should be protected for pulpwood.

SUMMARY

An ecological subdivision of the Upper Peninsula Experimental Forest at Dukes, Michigan, was made in order to obtain a physical basis for carrying on intensive silvicultural management and investigations. Natural elements of topography, such as hill tops, slopes, valleys, basins, areas with a high water table, and areas subject to overflow were blocked out. Five soil types were mapped; viz., (*a*) slightly podzolized loam, (*b*) loamy podzol, (*c*) swampy podzol, (*d*) muck, and (*e*) woody peat. Soils were correlated with forest growth and herbaceous vegetation, and five soil-forest sites recognized. They are:

SOIL TYPE	FOREST TYPE	FLORISTIC TYPE	PRODUCTIVITY
Slightly podzolized loam	Upland Hardwood Type (sugar maple, basswood, elm, etc.)	Acer-Nudum	High
Loamy podzol	Hemlock-Hardwood Type (hemlock, yellow birch, sugar maple, etc.)	Clintonia-Lycopodium	Medium to high
Swampy podzol	Lowland Hardwood Type (sugar maple, red maple, yellow birch, elm, black ash, balsam fir, white spruce)	Fern Type	Low
Muck	Hardwood-Conifer Swamp Type (red maple, aspen, yellow birch, white spruce, black spruce, balsam fir, tamarack, alder, and willow)	Urtica-Gallium	Low
Woody Peat	Cedar Swamp Type (white cedar, balsam fir, spruce, and some hardwoods)	Oxalis	Very low

Upon the basis of the information obtained, the experimental area was subdivided into ecologically uniform compartments, their boundaries were surveyed and blazed, and maps were prepared. This subdivision insures that future differences in composition and growth of stands will result specifically from silvicultural treatment, and not from the co-influence of soil and physiographic features. Thus, a safe, broad application of the results of these treatments becomes possible, and since permanent profile records were made during the course of this study, the influence of soil upon different cuttings, thinnings, and plantings can be observed, as well as the influence of different silvical treatments and tree species upon the soil itself.

REFERENCES

(1) GLINKA, K. D. 1927 The Great Soil Groups of the World and Their Development. Translated by C. F. Marbut. U. S. Dept. Agr.
(2) HESSELMAN, H. 1926 Studies of the humus layers of coniferous forests, their peculiarities and their dependence upon silviculture. *Meddel. Statens Skogsförsökanst.* [Sweden] 22: 169–552.
(3) JOFFE, J. S. 1931 The process of podzolization. *Soil Sci.* 32: 303–323.
(4) MUELLER, P. E. 1887 Studien über die natürliche Humusformen. Berlin.
(5) RICE, TH. D., AND GEIB, W. G. 1905 Soil survey of Munising area, Michigan. U. S. Dept. Agr. Advance Sheets: Field Operations of the Bureau of Soils.
(6) SEELEY, DEWEY A. 1922 Michigan Agriculture: 3. Climate. Mich. State Dept. Agr.
(7) STEBUTT, A. 1930 Lehrbuch der allgemeinen Bodenkunde. Berlin.
(8) United States Department of Agriculture 1905 Terms used in forestry and logging.
(9) VEATCH, J. O. 1928 Profiles of soils in the Great Lakes' region of the United States. *Proc. and Papers First Internatl. Cong. Soil Sci.* 5: 350–357.

PLATE 1

SOILS OF THE UPPER PENINSULA EXPERIMENTAL FOREST

(a) Slightly podzolized loam, (b) loamy podzol with ortstein, (c) swampy podzol with ortstein and gley, (d) swampy podzol without ortstein, (e) muck upon alluvial sand, (f) muck upon morainic drift, (g) woody peat.

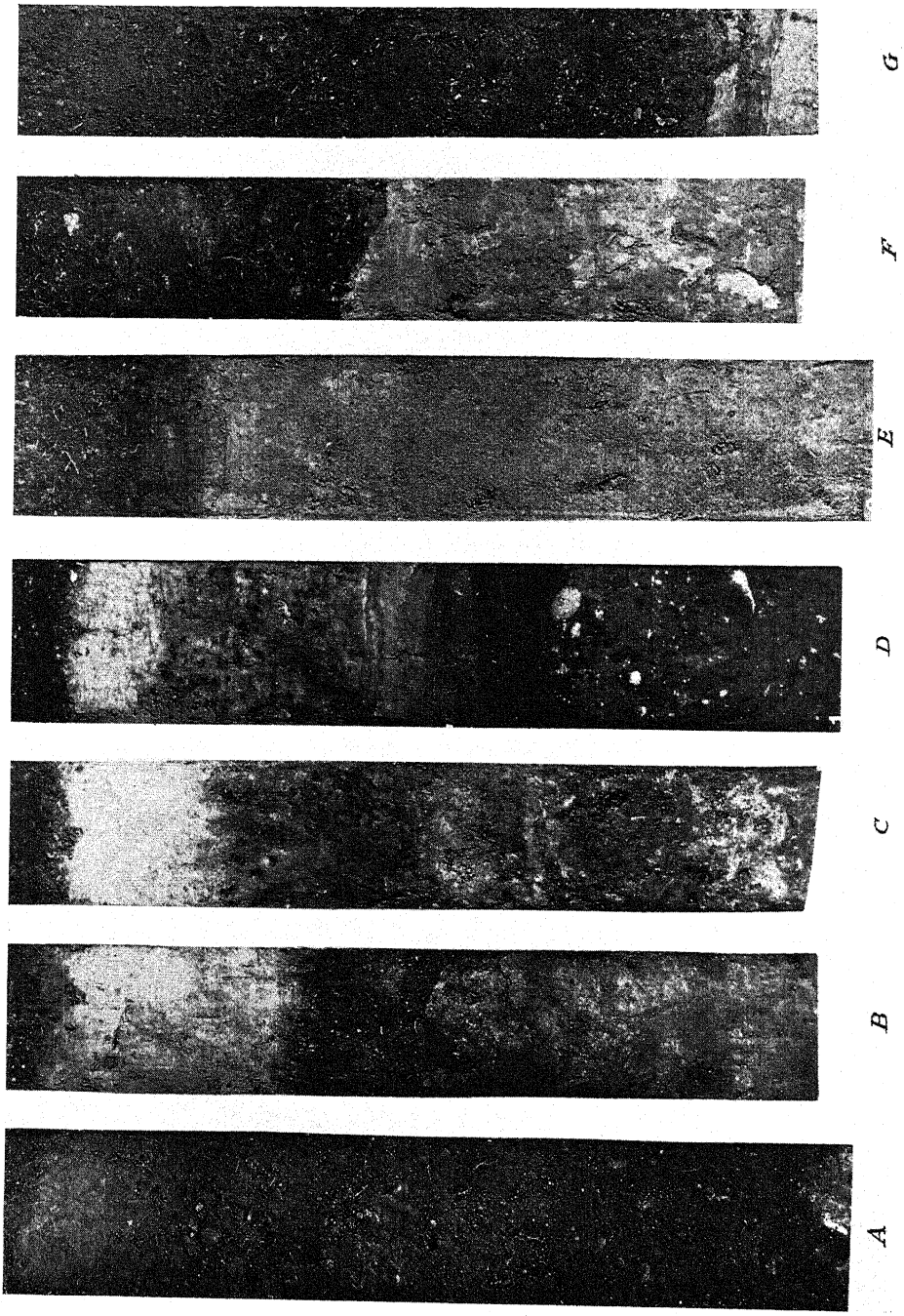
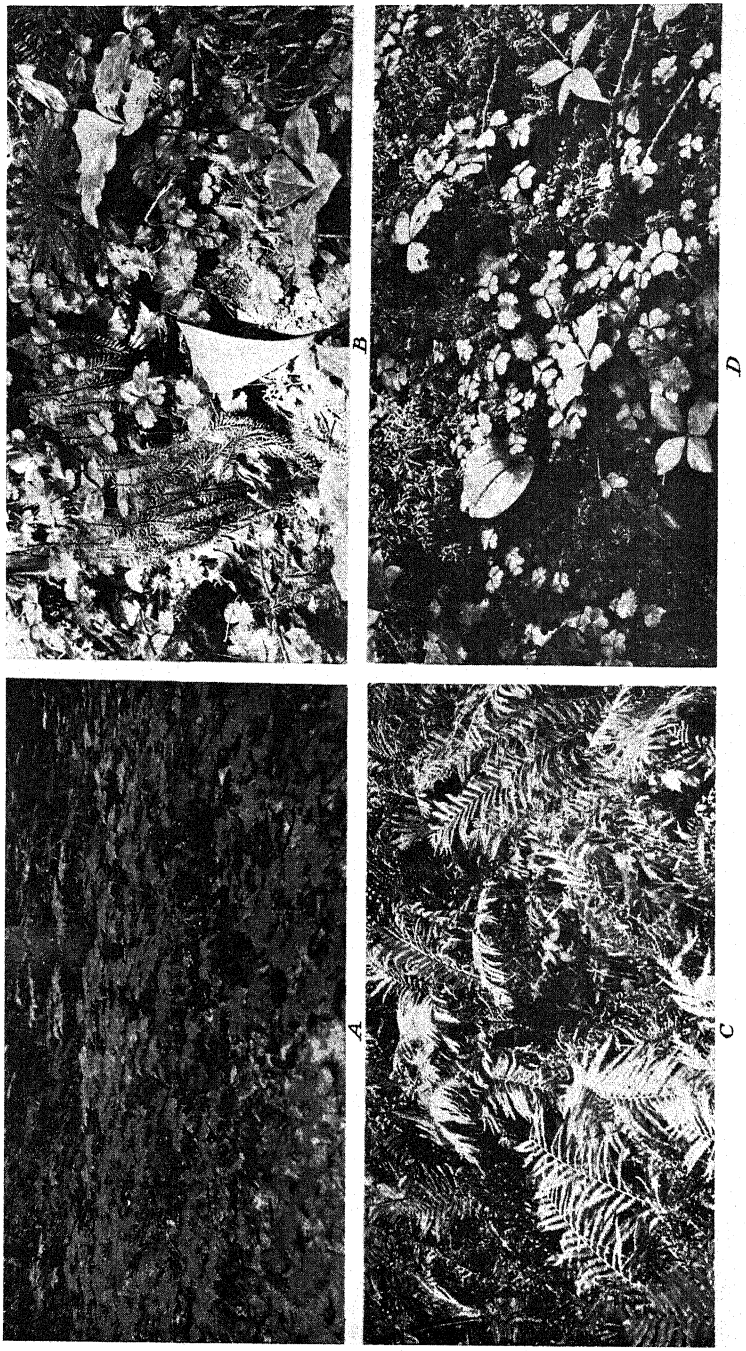

G
F
E
D
C
B
A

PLATE 2

GROUND VEGETATION OF THE UPPER PENINSULA EXPERIMENTAL FOREST

(a) Acer-Nudum type, (b) Clintonia-Lycopodium type, (c) fern type, (d) Oxalis type


B
D
A
C

THE MICROFLORA OF KAZAKSTAN SANDS (CENTRAL ASIA)

E. E. PAULIE

Medical Institute, Stalino, Donbass, U. S. S. R.

Received for publication December 21, 1933

One of the problems of the microbiological division of the Kazakstan Experiment Station of the institute for scientific investigation and study of India rubber was to investigate the microflora in the rhizosphere of the rubber-producing *Chondrilla ambigua, Ch. pauciflora, Ch. brevirostris*. Microbial counts were made by the Winogradsky method to determine the fluctuation in the number of microbes with the soil depth up to the point where the Chondrilla roots begin to branch out.

It was found expedient to reduce the amount of the fractions required by the Winogradsky method from 5 to 3 gm. In place of three sediments and two suspensions, two and one respectively were prepared by shaking 1 gm. of soil in 30 cc. of water and distributing the mixture in three test tubes. The other departure from the Winogradsky method consisted in increasing the number of counts. Instead of 20 fields, 50 were counted. Whenever the original count was questionable it was repeated.

The root system of Chondrilla proved to be extremely long and complicated, reaching the ground waters. The roots constantly change their direction, turning round an axis, making loops and all kinds of bends. At a certain depth, two or three long side roots branch out from the central root in a very irregular and tangled manner. The main root, like the side ones, looks like a long whip with a number of branches. These roots are easily broken and, remaining in the sand, render the work very difficult.

The depth of the water table varies with the topography. In the steppe it is generally found at a depth of 300 to 350 cm. but in low places and in the hollows of sandy hillocks (sand drifts not fastened by the vegetation) it is not lower than 200 cm. The distance from the top of a sandy hillock to the water table is 5 to 6 meters, depending on the height of the hillock. In general, however, the level of the water table does not fluctuate greatly on a smooth topography.

In its upper layers the soil is penetrated by the roots of various plants. The roots of most of the plants, except Chondrilla, stop at a depth of 50 to 70 cm. The entire main root of Chondrilla is covered with smooth brown cuticle which, together with the absence of short side roots, indicates that it does not utilize the moisture of the upper layer of the sand, as do the roots of other plants. The central root with its few long side rootlets, which are also covered with cuticle, branch out upon reaching the water table.

The soil samples were usually taken with sterilized aluminum tumblers near the root or from the root itself, the sand from which was shaken directly into an aluminum tumbler. If the root was lost, the soil sample was taken from the walls or the bottom of a pit. Sometimes a botanical scoop that had been wiped with a piece of sterilized cotton dipped in alcohol was used. Generally, the soil samples were sifted through a 1-mm. sieve. The samples taken near or from the water bearing layer, however, were not sifted as they represented liquid mud. The samples were examined during the first 2 or 3 days. The pH, determined colorimetrically by the Michaelis method, fluctuated from 7.5 to 8.5 but more often between 8.0 and 8.5.

The temperature of the water-bearing layer was found to be 12°C.; at 20 cm. above the water-bearing layer it was 14°C. The temperature of the superficial layer varies with the temperature variations of the air.

The results of the microbial counts lead to the following conclusions. There are two maxima; one near the surface at a depth of 5 to 20 cm., the other near the water-bearing layer at a depth of 175 to 200 cm. The bacilli often surpass the cocci in numbers. At the same time the numbers of bacilli and Azotobacter-like cells change more or less regularly with depth, and their quantity depends upon the general number of microbes. The number of cocci varies irregularly; sometimes the cocci are completely absent. The counting of other forms is generally difficult because many of them cannot be fixed with alcohol (spores) or they are destroyed during the fixation (infusoria).

Sometimes an unexpected rise or depression was noted in the number of microbes at a certain depth. For instance, in the second pit (table 1) there was a comparatively large increase at a depth of 85 cm.; in the fifth pit[1] a depression in the number of microbes at a depth of 130 cm. was observed; in the seventh, an unexpected increase in the numbers was noted at a depth of 110 cm.; in the eighth pit the increase was observed at a depth of 100 cm. Disregarding the fluctuations, there appeared, with sufficient clarity, two maxima as noted in the foregoing.

The low count of the superficial maximum and decrease in the upper layers of the soil of the sixth pit may be explained partly by the influence of the season; the pit was dug on July 30, when the upper layers are more likely to suffer from effects of desiccation. In the seventh pit, which was dug in shifting sands, the upper layers were not investigated because of the crumbling and also because of the seasonal influence manifested when digging was completed, on August 9. The season also influenced the superficial maximum at a depth of 20 cm. of the second pit, which also was dug in shifting sands just after the May rains on June 3. The third pit was also made in shifting sands.

Some fluctuations in the number of microbes at different depths also may be explained by the season of digging. The pit dug in May, because of the rains, shows an upper maximum nearer the surface than does the pit dug in August

[1] Although detailed information was obtained on eight pits, data on only four pits are presented in table 1 for purposes of illustration.

TABLE 1

The number of microbes in 1 gram of soil

DEPTH	TOTAL NUMBER OF MICROBES	BACILLI	COCCI	AZOTOBACTER-LIKE CELLS	OTHERS
cm.	*thousands*	*thousands*	*thousands*	*thousands*	*thousands*
		First pit			
5	30,675		3,500	27,000	175
15	22,000	2,500	5,000	14,000	500
30	7,300	1,300		6,000	
65	13,000	5,000	2,500	5,500	
105	28,400	10,500	1,500	8,000	8,400
		Second pit			
20	39,000	9,500	500	27,000	2,000
35	10,000	1,500		7,500	1,000
55	42,000	5,000	6,000	27,000	4,000
85	86,000	11,500	26,000	42,000	6,500
105	28,600	4,500	20,500	3,500	100
120	20,700	2,000	10,000	8,000	200
135	25,200	6,000	9,000	10,000	200
165	53,300	13,000	9,000	31,500	300
195	28,000	8,000		19,000	1,000
		Sixth pit			
5	14,000	3,000	500	10,000	500
30	6,000	1,000		3,000	1,500
50	39,000	22,000	8,000	7,500	1,500
60	14,500	6,000	1,500	5,000	2,000
(A)100	13,000	9,500	500	2,000	1,000
(B)100	21,000	9,000	4,500	7,000	500
140	19,000	4,500	1,000	12,000	1,500
180	23,500	9,000	1,500	10,500	2,500
255	45,500	7,500	2,000	33,500	2,500
300	19,000	2,000	2,500	13,500	1,000
320	40,500	8,500	3,000	29,000	200
345	11,000	6,000	500	3,000	1,500
		Eighth pit			
5–10	70,000	6,000	13,000	41,000	10,000
20–25	36,500	3,500	3,500	29,000	500
60	28,500	4,000	1,000	22,000	1,500
100	73,000	4,500	26,500	41,000	1,000
130–140	53,000	5,000	6,000	36,500	5,500
(A)170	39,500	2,500	1,500	20,000	15,500
(B)170	60,000	11,000	2,500	44,500	2,000
200	62,000	26,000	6,000	25,000	5,000
250	81,000	22,000	2,500	52,500	4,000
300	51,000	17,500	4,000	20,000	9,500

when the upper strata of the soil had dried out considerably. The lower maximum appears on the average at the 200-cm. depth. The third pit, having a depth of 350 cm., did not reach the water-bearing stratum; its maximum is at the 200-cm. depth. In the fourth pit, where the water-bearing layer is at a depth of 275 cm., the maximum is at the 200-cm. depth. In the fifth pit, where the water-bearing layer is at a depth of 175 cm., the maximum is at depths of 100 and 175 cm. The maximum at the depth of 175 cm. coincides with the water-bearing stratum. The proximity of the water-bearing layer to the surface may create such conditions of aeration and temperature that the maximum appears at the water level. In the sixth pit, where the water-bearing stratum is at a depth of 375 cm., the maximum is at a depth of 255 cm. In the seventh pit the lower maximum again coincides with the water-bearing layer at a depth of 200 cm. In the eighth pit the water-bearing layer is at a depth of 300 cm., and the lower maximum is at a depth of 250 cm. This is a typical position of the lower maximum in the strata overlying the water-bearing layer. Except for the fifth and seventh pits, the lower maximum does not coincide with the water-bearing layer.

Sometimes the roots do not reach the water-bearing stratum, terminating slightly above it. In the sixth pit the fine rootlets terminate at a depth of 345 cm., 20 or 30 cm. above the real water-bearing stratum. In the eighth pit the rootlets reached a point in the soil where it appeared like mud. The last deep samples had to be taken outside of the root zone.

In order to clarify the assertion that Chondrilla exerts effects on the quantitative composition of the microflora in the rhizosphere, a seventh pit was dug, known as the "empty pit," since the excavation was not done along the rhizosphere. Around a Chondrilla bush a simple wide pit was dug in the usual manner. The roots were cut by the spade with the walls of the pit at a distance from the bush and not in contact with the root system. The only departure from the normal was the fact that the maximum coincided with the water-bearing stratum, which might be explained by the nearness of the water-bearing layer to the superficial soil layers from which it was separated by a distance of 200 cm. The same results are apparent in the fifth pit where the digging was accomplished along the root and where the lower maximum also coincided with the water-bearing layer at a depth of 175 cm.

One common trait of the fifth and the seventh pits was that both were dug in the middle of a circle of sand hillocks, in a place where the water table was lower than usual for the steppe. From the numbers showing the change of microbes according to the depth, it is impossible to guess which of the pits was dug along the rhizosphere and which was dug outside of it. The coincidence of the maximum in microbes in relation to the water table points to the conclusion that both pits were dug under the same conditions of soil topography. Each pit, in certain parts, proved to be an "empty one"; in the process of digging sometimes not only the rootlets were lost, but also the medium parts of the root. That is why one could foretell that there would be no substantial

difference between the empty and normal pits, just as there was no difference between the layers close to the rhizosphere and those out of contact with it.

In the sixth pit at a depth of 100 cm., one sample of soil from the principal root was taken with a scoop, and a parallel sample was taken from the vertical wall of the pit not in contact with the root. In the soil sample taken along the root there were 13,000,000 bacteria and in the sample from the wall 21,000,000. In the eighth pit at a depth of 170 cm., sample A (table 1) was taken out of contact with the rhizosphere, the dark spongy mass also being taken with it. Sample B was taken from the root and beside the root. Sample A contained 39,500,000 microbes, sample B, 60,000,000 microbes, just the reverse of the data obtained from the sixth pit. The smaller number of microbes found on the wall of the pit was probably due to the inclusion in the sample of the dark mass, which, according to the experience with the fifth pit, contains a negligible number of microbes.

The numbers of microbes at the various depths lead to the conclusion that the rhizosphere of Chondrilla does not appreciably influence the microflora of the surrounding soil. If it did, the data on the number of microbes in the different strata of the soil would not show the marked changes due to seasonal differences. All of the root is covered with cuticle which excludes the influence of enzymes on the surrounding soil. There is a possibility, however, that Chondrilla influences the quantity of microbes in the rhizosphere of the rootlets where diffusion of the fermenting juices from the cells is possible. But just at the termination of the root zone the maximum of microbes is not observed, because these root endings are dipped in the water-bearing layer. Evidently the low temperature and a hampered condition of aeration do not favor a rich development of microbes in the region of root endings.

The experiments described in this paper, when examined by the indexes laid down by Winogradsky, do not indicate that Kazakstan soils have a richly populated microflora. Winogradsky recognizes three kinds of soils: (*a*) soils with a rich microflora which contain more than 1 milliard of microbes in 1 gm. of soil; (*b*) the medium soils, which contain not more than 1 milliard in 1 gm.; and (*c*) the poor soils, which contain not more than 0.5 milliard of microbes in a gram of soil. From this point of view, the Kazakstan soils, in which only some tens of millions of microbes were found in a gram of soil, must be considered as poor.

The microflora is classified by the Winogradsky method into bacilli, cocci, Azotobacter, etc. In these experiments the microbiologist will doubt the presence of Azotobacter in the deep layers. Of course the morphological similarity alone is not enough evidence that the organisms are Azotobacter cells. At this point, however, it is well to recall the work of Kononova,[2] who

[2] M. M. Kononova. The vertical distribution of Azotobacter and nitriferous organisms in the soils of certain districts of Central Asia. The collection of works of the microbiological department of the laboratory investigations of AK-Kavak's experimental station of irrigation, issue 7th.

found Azotobacter in the soils of Bukhara at a depth of 2 meters. Kononova considered cultivated soils where Azotobacter penetrated great depths. The soils of the Irrigation Experiment Station have been under irrigation for centuries. In Kazakstan the problem is more complicated because the experiments were conducted on the semi-desert soils which have never been worked before. How the Azotobacter penetrated these soils is not at all clear.

It is interesting to note that preparations made of other Kazakstan soils, Mouiun-Kooms, Kara-Kooms, and Kurtins sands, show characteristics similar to those recorded in these experiments. They contain many bacillary forms, few cocci, and cells resembling Azotobacter. The latter were also found in the preparations of the samples of soil sent from the hills of Kara-Tohand. It was there that the eudemic rubber-bearing tan-Saghyz was discovered.

Future experiments will show whether the so-called Azotobacter organisms are capable of fixing nitrogen. Kononova, who isolated Azotobacter from the deep soil layers, states: "The presence of Azotobacter at such a depth is incompatible with our usual notion about it as an aerobic organism." Heinze maintains that there is no soil without Azotobacter. Shulgina[3] points out that the virgin soils of Turkestan contain as many Azotobacter organisms as the cultivated soils.

A question was raised as to the accuracy of the Winogradsky method. The experiments recorded do not answer this question. The method presents considerable difficulties. The least of these is the washing off of the first sediment and the greatest is the ability to remove from the 10 cc. of liquid a drop which will contain a representative quantity of microbes for the given fraction. Many bacteria are adsorbed by the soil particles and in such a case they are not noticed at all or are seen dimly and cannot be counted. One must agree with Shulgina and her collaborators that the numbers obtained by direct microscopical methods are considerably reduced, as it is impossible exactly to discern separate species among the groups of bacteria adsorbed by the soil particles. In comparison with other methods the direct microscopic method, in spite of all its defects, gives the numbers more correctly than, for instance, the plate method.

The microbiological investigation of the Kazakstan sands shows that even those semi-desert sands are not free from a definite microflora.

[3] Shulgina, Berseneva, and Norkina 1930 Materials to microbiological characteristics of the Turkestan soils. *Works of the Institute of Agricultural Microbiology*, vol. 4. Omelianskiy 1915 About the spread of nitrogen fixing bacteria. *Arch. Biol. Sci.*, vol. 18.

STUDIES ON TROPICAL SOIL MICROBIOLOGY: II. THE BACTERIAL NUMBERS IN THE SOIL OF THE MALAY PENINSULA

A. STEVEN CORBET[1]

Agricultural Research Station, Jealotts Hill, England

Received for publication November 23, 1933

In the last decade, in both Europe and America, increasing attention has been paid to the enumeration of the microörganisms in the soil. Such work has usually been carried out by the plate-counting method, the reliability of which has been investigated, under temperate conditions, by Fisher, Thornton, and Mackenzie (5) in England and by Waksman (12, 13) in America. This method has its limitations, but, by its use, fairly reliable estimates can be obtained of the numbers of certain groups of aerobic microörganisms present in the soil. It need hardly be stressed, however, that results obtained from a few isolated determinations may be totally misleading.

As a result of investigations by the aid of the plate-counting method by Cutler, Crump, and Sandon (4) and by Thornton and Gray (11) at Rothamsted, the seasonal and diurnal fluctuations normally occurring in the numbers of soil microörganisms appearing on the agar plates are fairly well known for temperate regions. There is general evidence that bacterial numbers and activities are greatest during the spring and autumn, and it is also apparent that, in general, there are two maxima during the day, one occurring about 10 a.m. and the second in the evening. It might be anticipated that variations in the numbers of soil microörganisms would be closely related to the temperature and moisture-content of the soil, but definite evidence on this matter is lacking. Thornton and Gray (11) could find no correlation between changes in bacterial numbers and the soil moisture-content, and but rarely were soil temperature changes reflected in fluctuations in the bacterial population: this investigation, however, was primarily concerned with diurnal variations. If the fluctuations in the numbers of soil microörganisms are largely the reflection of variations in the temperature and soil moisture-content then, in equatorial regions such as Malaysia where the monthly variations in temperature are negligible and the rainfall is high and, under usual circumstances, soil moisture cannot become a limiting factor, it would be anticipated that the numbers of soil microörganisms present per unit of soil would approach a constant value. As far as could be traced no systematic work of this nature

[1] This investigation was carried out at the Rubber Research Institute of Malaya by the writer in his capacity of bacteriologist. Thanks are due to the director of the institute for permission to publish the results.

had been carried out in the tropics previously and it appeared highly desirable to investigate this matter when the opportunity presented itself.

A further reason for examining the fluctuations in population of soil micro-organisms under tropical conditions is that variations in the numbers are often invoked to explain certain changes which follow the felling and clearing of tropical forests. Since many of the statements found in the literature concerning the biological changes consequent upon clearing are highly speculative, the subject merits scientific investigation.

THE SUNGEI BULOH EXPERIMENT

In the early months of 1929 a large plot (block 15) on the Experiment Station of the Rubber Research Institute of Malaya at Sungei Buloh, Selangor, F. M. S., was cleared of primeval forest and subsequently planted with rubber seedlings and a leguminous cover. During 1929 and the year following soil samples were taken at approximately weekly intervals, and the numbers of microörganisms per 1 gm. of moist soil were determined by the usual plate-counting method. Sampling was always carried out at 10 a.m. when the bacterial population of the soil is considered to reach a maximum. Each week two samples of soil were taken from random sites on block 15: the surface soil was scraped off and a sample was taken to include the layer from 1 to 4 inches below the surface. Plates were poured when the samples were precisely 24 hours old, and Thornton's mannite-agar medium (10) was employed. Three or four plates, latterly always four, were poured for each sample. At first dilutions were made of 1/1,000, 1/10,000 and 1/100,000, but since it was found that the 1/1,000 dilutions were always countable, the higher dilutions subsequently were omitted. All colonies were counted and, in this paper, the term "bacterial counts" must be understood to comprise fungi and actinomyces, as well as bacteria. The plates were incubated at laboratory temperature (26°–29°C.) for 5 days before counting. Preliminary trials showed this period to be the optimum for the purpose as longer incubation resulted, not in the appearance of further colonies, but in the overgrowth of certain fungal colonies.

Briefly, the history of block 15 is as follows: The virgin forest was felled in March 1929, and the timber and brushwood were roughly collected into heaps and burnt. In the latter part of March and during April the rainfall was heavy and a condition almost approaching water-logging obtained: efficient drainage was not completed until October. "Burning-off" operations first took place in the beginning of June and then, after a lapse of 3 weeks or so, were resumed in the middle of July and continued until well into September. From November onwards a cover of a low-growing leguminous plant, *Centrosema pubescens*, was established and seedlings of *Hevea brasiliensis* were planted in December. In the latter half of 1930 the growth of the cover was luxuriant and the soil was strongly shaded. It is to be regretted that more counts were not made while the soil was under forest, but this unavoidable omission was in some measure rectified by occasional sampling from the forest reserve surrounding the experiment station.

The most striking of the general climatic features of the Malay Peninsula are the uniform temperature and high humidity [see Haines (6) where meteorological records are discussed from the viewpoint of the agriculturist]. The only noticeable seasonal variations are slight differences in the rainfall, definite maxima occurring about April and November; but the wettest period of the year usually ranges from October to January. The annual rainfall is over 100 inches and the rainfall intensity may often be considerable.

The mean air temperature is approximately 80°F. with a range of about 3°. In virgin forest the soil temperature is 75°F., the daily variation at the surface being less than 1°. On the other hand, Haines found that the mean soil temperature under bare ground at the experiment station was some 6° to 15°F.

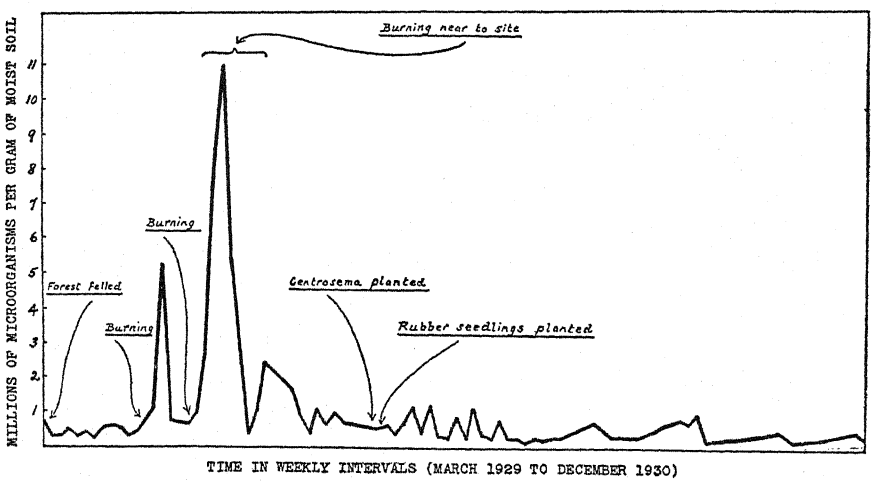


FIG. 1. FLUCTUATIONS IN BACTERIAL NUMBERS ON BLOCK 15 OF THE SUNGEI BULOH EXPERIMENT STATION DURING THE CONVERSION OF VIRGIN FOREST INTO A RUBBER PLANTATION

higher, the greatest daily range found being 35° and, on occasions, the soil temperature at the surface rose to well over 100°F. A diminution of some 3° or 4° in the mean temperature of the soil surface was produced by the cultivation of a low-growing cover plant.

The relative humidity of the atmosphere is usually over 90 per cent of the saturation value, but it may fall to figures in the sixties during the warmer hours of the day.

It became evident in the earlier stages of the experiment that the proportion of fungi to bacteria is much higher, and the total numbers of soil microörganisms found are considerably lower, than in temperate regions.

The results obtained for the counts on the Sungei Buloh plot are expressed graphically in figure 1. The points shown represent the geometric means for two samples taken at the same time on the same day, the value for each

sample being obtained by taking the arithmetic mean of the plate counts for the sample in question. This procedure is recommended by Robertson (9) and has much to commend it; reference will be made to this matter, however, later.

From figure 1 it is evident that the results were uniformly low throughout the 2 years except for short periods following the "burning-off" operations when large increases in the population were found. Usually the effects of a burn-off were localized but, on occasions, the wood-ash was wind distributed. That the increased population is attributable to the presence of wood-ash and not to any "partial sterilization" effect produced by the fires is certain because high counts were obtained on sites where the wood-ash had been blown by the wind, and also under the site of an actual fire on the day following burning. This rise in numbers was evanescent, and conditions returned to normal very soon after actual burning operations ceased. The explanation of the high counts appears to be not entirely a question of neutralization of an acid soil (the pH of the Sungei Buloh soils was usually below 5.0) but also a matter of base exchange. An experiment was carried out in which wood-ash, containing 6.99 per cent potassium, was added to Sungei Buloh soil in a plant pot in the laboratory and at intervals the soil was watered with distilled water in amount corresponding to the normal rainfall. Altogether 12.39 gm. of potassium were added to the soil, but only 0.42 gm. was recovered in the drainage water after 27 days. On the other hand, it is clear that the increased population is not directly due to the presence of potassium, for laboratory experiment showed that the rate of carbon dioxide production from the Sungei Buloh soil was quite unaffected by addition of potassium sulfate at the rate of 5 cwt. per acre.

The results of the Sungei Buloh experiment show that the microbiological population of the soil remains approximately constant throughout the processes of felling, clearing, and planting, and only as a result of drastic burning operations are the numbers of soil microörganisms materially affected. For the greater part of 1929 the soil was uncovered and exposed to the tropical sun, whereas during the latter part of 1930 it was shaded by a dense growth of *Centrosema pubescens*, a change of treatment which has not been reflected in fluctuations in the numbers of soil microörganisms present.

In table 1 are given the distribution frequencies of the results of the Sungei Buloh experiment, and when these are expressed graphically a J-shaped curve is obtained.

If, instead of taking the actual figures for the counts, the logarithms of these values are used, the plot of the distribution frequencies is a bell-shaped curve, characteristic of a population normally distributed, but there is, in addition, a smaller curve containing classes of higher values (table 2). These high values falling outside the principal curve were all obtained during the period when "burning-off" operations were in progress and there can be no doubt that they are to be attributed to the presence of wood-ash on the soil. The results clearly indicate that the slight variations found in the bacterial counts from

soil on the experiment station throughout the 2 years are of little significance except in the case of the samples taken during the period of burning operations. No correlation was found between numbers of microörganisms and rainfall.

TABLE 1

Distribution frequencies of the bacterial counts from the soil on Sungei Buloh Experiment Station, 1929–1930

THOUSANDS OF MICROÖRGANISMS PER 1 GRAM OF MOIST SOIL	FREQUENCY
0– 200	21
201– 400	31
401– 600	29
601– 800	18
801–1,000	7
1,001–1,200	7
1,201–1,400	3
1,401–1,600	4
1,601–1,800	0
1,801–2,000	2
2,001–2,200	0
2,201–2,400	1
2,401–2,600	0
2,601–2,800	1
2,801–3,000	0
Above 3,000	10

TABLE 2

Distribution frequencies of the logarithms of the bacterial counts from the soil on Sungei Buloh Experiment Station, 1929–1930

LOGARITHMS OF THOUSANDS OF MICROÖRGANISMS PER 1 GM. OF MOIST SOIL	FREQUENCY
1.61–1.80	1
1.81–2.00	1
2.01–2.20	6
2.21–2.40	20
2.41–2.60	24
2.61–2.80	31
2.81–3.00	24
3.01–3.20	13
3.21–3.40	3
3.41–3.60	2
3.61–3.80	5
3.81–4.00	3
4.01–4.20	0
4.21–4.40	0
4.41–4.60	1

Microbiological examination of other soil samples in the Malay Peninsula

A number of soil samples were taken from various other sites in the Malay Peninsula (primary and secondary forest, mangrove forest, coastal peat soil, garden soil, and other rubber estates), and the numbers of microörganisms developing on the plates were determined in precisely the same manner as before. The results obtained on the experiment station were confirmed: in general, the total numbers were low, almost invariably fungi predominated over bacteria and, curiously enough, in three of the four instances where values of over 1 million were found, earthworms were present. The earthworm, *Pontoscolex corethrurus* Fr. Müll., is by no means abundant in Malaya and it was found on but few occasions during the course of soil sampling.

TABLE 3

Distribution frequencies of the logarithms of all the bacterial counts obtained in the Malay Peninsula

LOGARITHMS OF THOUSANDS OF MICROÖRGANISMS PER 1 GM. OF MOIST SOIL	FREQUENCY
1.61–1.80	1
1.81–2.00	4
2.01–2.20	11
2.21–2.40	30
2.41–2.60	37
2.61–2.80	38
2.81–3.00	30
3.01–3.20	15
3.21–3.40	4
3.41–3.60	2
3.61–3.80	5
3.81–4.00	3
4.01–4.20	0
4.21–4.40	0
4.41–4.60	1

A feature of the investigation was the almost complete absence of colored colonies on the plates. One species, *Rhodococcus prometheus* Cbt. (2), found in forest soil on one occasion only, produced a pigment which was carmine-red in acid, and yellow in alkaline solution, the change being reversible.

As in the case of the experiment station results, for each sample the arithmetic mean of the respective plate counts has been calculated and the distribution frequencies of the logarithms of the whole of the counts obtained in the Malay Peninsula (i.e. those from the experiment station plus all the others) are given in table 3. The histogram is characteristic of a normally distributed population if some eight or nine high values be excepted. These high results, which ranged between 4,800 and 30,000 in actual values, were all taken during the period of "burning-off" operations on the experiment station.

The results emphasize the advantage of employing the logarithmic and not the arithmetic values of the counts. The arithmetic mean of the experiment station results is 1,168,000, whereas the geometric mean is 557,000. It is evident that the latter value must be much nearer the true mean. The arithmetic mean of the whole of the Malayan counts is 969,000, whereas the geometric mean is 469,000.

The growth of microörganisms takes place according to the bacterial growth curve, and the writer (1) has suggested that this cycle has a much wider application than is generally realized. The normal growth curve is divisible into a number of more or less clearly defined phases: following the initial period of slow growth (phase of adjustment) is a period of rapid growth (phase of increase) which is maintained until the stationary phase of crisis is reached; after this a period of decline sets in and the phases of decrease and readjustment can be recognized. Of these growth periods, the phases of increase and decrease are the most important, for, normally, they are of longest duration and in each case the rate of growth bears an exponential relation to the time. The writer (3) has shown, as a result of work on the evolution of carbon dioxide from soils in the laboratory, that the period between removing the sample from the field and examining it in the laboratory corresponds to the phase of decrease on the bacterial growth curve, during which the decline in numbers is strictly logarithmic. This being so, it is evident that Robertson's suggestion that bacterial counts should be averaged by taking, not the arithmetic, but the geometric mean is based on sound premises.

If the distribution frequencies of the whole of the actual bacterial counts obtained in this investigation are plotted, the values fall on a J-shaped curve and the arithmetic mean of all the results does not coincide with the mode of the curve. On the other hand, in the curve showing the distribution frequencies of the logarithms of the counts the value for the mean of all the samples coincides almost exactly with the mode of the curve, the absence of complete agreement being attributable to the presence of samples taken during "burning-off" operations which pertain to a different population. It may be worth pointing out that the distribution frequencies of the 60 plate counts obtained by Waksman (12, p. 91) for the same soil sample, when plotted, form a skew curve but the plot of the distribution frequencies of the logarithms of these values gives a normal curve in which the mean of the values corresponds to the mode of the curve.

A statistical examination of the data reveals that, although the values obtained on the Sungei Buloh experiment during the period of "burning-off" operations (June to September 1929) are significantly greater than those found during the remainder of the experiment, these latter are not significantly different from the values found for 10 samples from virgin forest. The relevant data are:

	NUMBER OF SAMPLES	MEAN VALUE OF LOGARITHMS OF RESULTS	STANDARD ERROR OF LOGARITHMS OF RESULTS
(*a*) Sungei Buloh Experiment (excluding burning period)	109	2.609	0.0283
(*b*) Sungei Buloh Experiment ("burning-off" period)	27	3.275	0.0878
(*c*) Virgin forest	10	2.553	0.104

At the $P = 0.05$ level of significance, the mean of (*b*) is significantly different from the means of both (*a*) and (*c*), there being no significant difference between these last two.

Calculation of Pearson's constants β_1 and β_2 for the logarithmic values of all the 156 bacterial counts on soils in the Malay Peninsula, other than those carried out during the "burning-off" period at the Sungei Buloh Experiment Station, has shown these to be 0.0001 and 2.57 respectively. For a symmetrical distribution β_1 is zero while β_2 is 3.0 for a normal curve but is smaller or greater according as the curve is platykurtic or leptokurtic. For the logarithmic values of the 60 bacterial counts obtained by Waksman for the same soil sample, referred to in the foregoing, β_1 and β_2 have the values 0.0711 and 2.58. The logarithms of the 30 counts made by Eggleton (4a) on a grassland plot at Jealotts Hill from March to November gave $\beta_1 = 0.0005$ and $\beta_2 = 2.84$ for bacteria and $\beta_1 = 0.0027$ and $\beta_2 = 2.11$ for fungi.

DISCUSSION

As a result of this investigation the important conclusion is reached that, under the usual conditions prevailing in the Malay Peninsula, the number of soil microörganisms in 1 gm. of soil (as determined by the plate-counting method) approaches a constant value of 500,000. This number is very low compared with the values found in temperate countries: for instance, the bacterial counts per 1 gm. of soil obtained by Thornton and Gray (11) for Rothamsted soils ranged between 8 and 50 millions and were usually in the neighborhood of 20 millions. The fact that no significant difference was found between samples taken from soil under virgin forest and from soil on clearings exposed to the sun may be of some importance, for it shows that an appreciable rise in the mean temperature has produced no measurable changes in the microbiological population of the soil.

These results have some bearing on the much debated question in tropical agriculture as to whether dead timber from areas recently cleared of forest should be collected and burnt, or allowed to remain on the site and decay. Almost invariably in Malaysia the timber is "burnt-off," but it is now known that some of the arguments employed by the advocates of this procedure are erroneous. Only one of these arguments need concern us here: it has been

submitted that, by permitting timber to decay on the site of clearing, a considerable amount of readily available soil nitrogen is locked-up as a consequence of the addition to the soil of material with a very high carbon nitrogen ratio. If such a locking-up of nitrogen in the body material of microörganisms occurred it would be reflected in an increased soil microbial population, but the results presented in this paper show that such population increases do not take place. Decaying timber is always present in the forest under natural conditions, and it is now known that the destruction of this material is affected almost entirely through the agency of termites. As a further advantage of "burning-off" it has been suggested that a temporary reduction in the numbers of soil microörganisms must follow this process of "partial sterilization:" this anticipation is entirely wrong.

The results reported here also throw light on a problem of fundamental importance. It has been shown that, under constant humidity factors, the nitrogen content of the soil decreases exponentially with increasing temperature (7, 8). In the Malay Peninsula, the soil temperature in the virgin forest is constant at 24°–25°C. but it may be raised very considerably when the forest is cleared and the soil exposed to tropical sunshine. It is well known that such exposure results in a reduction of the organic matter content as well as in a diminished nitrogen content. The question as to the mechanism by which this reduction of the nitrogen content of the soil is effected is of some importance: it is usually assumed that the increased soil temperature consequent upon removal of the shade of the forest results in increased microbiological activity which, in turn, accounts for the disappearance of readily oxidizable organic matter; but the results given here show that such an explanation cannot be upheld. It seems evident that the fall in the nitrogen content of the soil to a lower level on subjection to higher temperatures must be ascribed to chemical and not to microbiological agency, but this subject will be returned to in the next part of this series of papers.

SUMMARY

It is shown that, under the equatorial conditions prevailing in the humid tropics of the Malay Peninsula, the number of soil microorganisms, as determined by the usual plate-counting method, is constant under all normal conditions and approximates a value of 500,000. The results suggest that fluctuations in bacterial numbers in the soil are primarily functions of changes in the temperature and moisture content and when these factors are maintained constant no variations in bacterial numbers are apparent.

On almost all the plates examined fungi predominated over bacteria, indicating that these organisms play an important rôle in the decomposition of soil organic matter in the humid tropical regions.

The practical consequences of the results are discussed.

REFERENCES

(1) CORBET, A. S. 1933 The bacterial growth curve and the history of species. *Nature* 131: 61–62.

(2) CORBET, A. S. 1933 A new species of *Rhodococcus* found in the soil in the Malay Peninsula. *Centbl. Bakt.* (II) 88: 475–476.

(3) CORBET, A. S. 1934 Studies on tropical soil microbiology: I. The evolution of carbon dioxide from the soil and the bacterial growth curve. *Soil Sci.* 37: 109–115.

(4) CUTLER, D. W., CRUMP, L. M., AND SANDON, H. 1922 Quantitative investigation of the bacterial and protozoan population of the soil, with an account of the protozoan fauna. *Phil. Trans. Roy. Soc.* [London], *Ser. B* 211: 317–350.

(4a) EGGLETON, W. G. E. 1934 Studies on the microbiology of grassland soil. I. General chemical and microbiological features. *Jour. Agr. Sci.* 24: 416–434.

(5) FISHER, R. A., THORNTON, H. G., AND MACKENZIE, W. A. 1922 The accuracy of the plating method of estimating the density of bacterial populations. *Ann. Appl. Biol.* 9: 325–359.

(6) HAINES, W. B. 1931 Summary of meteorological results, Soils Division. Rubber Res. Inst. Malaya Bul. 4.

(7) HOCKENSMITH, R. D., AND TUCKER, E. 1933 The relation of elevation to the nitrogen content of grassland and forest soils in the Rocky Mountains of Colorado. *Soil Sci.* 36: 41–45.

(8) JENNY, H. 1929 The relation of temperature to the amount of nitrogen in soils. *Soil Sci.* 27: 169–188.

(9) ROBERTSON, A. H. 1932 Averaging bacterial counts. *Jour. Bact.* 23: 123–134.

(10) THORNTON, H. G. 1922 On the development of a standardised agar medium for counting soil bacteria, with especial regard to the repression of spreading colonies. *Ann. Appl. Biol.* 9: 241–247.

(11) THORNTON, H. G., AND GRAY, P. H. H. 1930 The fluctuations of bacterial numbers and nitrate content of field soils. *Proc. Roy. Soc.* [London], *Ser. B* 106: 399–417.

(12) WAKSMAN, S. A. 1922 Microbiological analysis of soil as an index of soil fertility: I. The mathematical interpretation of numbers of micro-organisms in the soil. *Soil Sci.* 14: 81–101.

(13) WAKSMAN, S. A. 1922 Microbiological analysis of the soil as an index of soil fertility: II. Methods of the study of numbers of micro-organisms in the soil. *Soil Sci.* 14: 283–298.

BOOK REVIEWS

Small-Fruit Culture. By JAMES SHELDON SHOEMAKER. P. Blakiston's Son & Co., Inc., Philadelphia, 1934. Pp. xv + 434, figs. 52.

The shift from crops of low to high commercial value per acre has run parallel to specialization and intensification of production. The New England and the Middle Atlantic States have paid increasing attention to the production of small fruits. There has been a rather remarkable expansion in small fruit culture in the Southeast and on the Pacific Coast. It is proper to expect that *Small-Fruit Culture,* offered as a text for instruction and reference work, as well as a guide for field practice, should be welcomed widely.

The author notes that "The text is based on information derived from the extensive but scattered literature; suggestions (heretofore unpublished) from specialists at various institutions; growers' experience; and, the author's own work with small fruits. The practical application is emphasized throughout the text."

The principal sections of the book relate to: Part I. Grape Culture; Part II. Strawberry Culture; Part III. Bramble-Fruit Culture; Part IV. Currant and Gooseberry Culture; Part V. Blueberry Culture; and Part VI. Cranberry Culture. There is a list of 389 references. Teachers in our colleges of agriculture, small-fruit growers, research workers, and others will feel indebted to the author for having brought together much useful material.

Commercial Flower Forcing. By ALEX LAURIE and L. C. CHADWICK. P. Blakiston's Son & Co., Inc., Philadelphia, 1934. Pp. x + 519, figs. 49.

Many new methods of floriculture have come into existence within the present decade. Progressive florists have not been slow in adopting the findings of our research workers in so far as technical data were ready for use in commercial floriculture. The notable progress which has been made by geneticists and plant physiologists, and likewise the contributions for which we are indebted to plant pathologists and entomologists, are playing a more important rôle in commercial floriculture than they did a few years ago. As indicated by the authors: "The object of this concise treatise is to cover the fundamentals involved in the growing of various flower crops used for commercial purposes and deal with them from the viewpoint of practical culture. The treatments recommended follow the routine practice of the better growers, supplemented by a vast volume of experimental work done under the experienced supervision of the authors."

The 27 chapters of the book deal with the following: Status and Development of the Industry; Plant Structures and Their Function: Greenhouse Con-

struction and Heating; Factors Influencing Plant Growth; Soils; Fertilizers; Reproduction; Diagnosing Greenhouse Ills; Major Crops; Minor Crops; Miscellaneous Cut Flower Crops; Bulbs, Corms and Tubers; Flowering Pot Plants; Foliage Plants; Forcing Hardy Plants; Outdoor Crops; Wholesale Marketing; Costs of Production.

The Biology of Bacteria. An Introduction to General Microbiology. By ARTHUR T. HENRICI. D. C. Heath and Co., Boston, etc. 1934. Pp. x + 472, figs. 112.

The present trend toward the better training of our research workers in the biological sciences is manifested in part by the publication of this book. In preparing the treatise, the author, as he himself notes, was guided by the wish to create something that would be "an introduction to general microbiology." In his own words: "This is a textbook to be used by general or nontechnical students who will take but one course in microbiology; or in introductory courses for other students who will be taught particular applications of the science in advanced courses." He says, further:" Above all, I have tried to present the material as *microbiology*, not as agriculture or hygiene—to stress the pure science aspects rather than the applications."

After reviewing the history of bacteriology, the author devotes a chapter to the microscope and microscopy. This is followed by five chapters on a survey of microbic life, devoted to the discussion of protozoa, algae, fungi, bacteria, and the ultramicrobes. The next six chapters are devoted, respectively, to the finer structure of bacterial cells; the growth and reproduction of bacteria; heredity and variation in bacteria; the metabolism of bacteria; the cultivation of bacteria, and the death of bacteria. Chapters XIV and XV are given over to a discussion of infection and immunity, respectively; and Chapter XVI is devoted to bacterial diseases of plants. Chapters XVII to XXIX deal with classification of bacteria; the nitrobacteriaceae; the coccaceae; the spirillaceae; the bacteriaceae; the bacillaceae; the mycobacteriaceae; the actinomycetaceae; the molds, yeasts, and yeast-like fungi; the pathogenic protozoa; the spirochaetales; and the rickettsia and virus diseases.

The work is sufficiently compact to favor its use in one-semester courses of collegiate credit. The author is to be commended for having presented clearly and effectively a subject in which there is a growing interest. The publishers have done their part in making the book attractive.

Commercial fertilizers. Their sources and use. By GILBEART H. COLLINGS. P. Blakiston's Son & Co., Inc., Philadelphia, 1934. Pp. xiv + 356, figs. 85.

The field of commercial fertilizers is a changing one in that new discoveries and technical improvements are calling for adjustments both among the manufacturers and the users of commercial fertilizers. The reader of this book will recognize how much change has occurred even within the last half dozen years in the fertilizer industry. New sources of raw materials have developed, and fertilizer practices have changed for economic as well as other reasons.

The author tells us that "The text is the outgrowth of the author's sixteen years of experience as an experiment station agronomist and teacher of soil, fertilizer and crop courses at the Clemson Agricultural College. For a number of years the subject matter included herein has been presented to classes composed largely of juniors and seniors." He states, further: "This book represents a composite of the opinions and conclusions of authorities within the fertilizer industry, as well as the conclusions of experiment station agronomists, especially in the fertilizer-using territory of the United States.

The book is made up of 15 chapters, dealing with the following subjects: Origin and Development of the Use of Commercial Fertilizers; Source, Production and Use of Sodium Nitrate; Manufacture and Use of Ammonium Sulphate; Manufacture and Use of the Synthetic Nitrogenous Fertilizers; Sources and Uses of Organic Nitrogenous Fertilizers; Sources and Use of the Mineral Phosphates; Sources and Use of Bone Phosphate and Basic Slag; Manufacture and Use of the Superphosphates; Production, Manufacture and Use of the German and French Potash Salts; Miscellaneous Sources of Potash Fertilizers; Sources and Uses of Fertilizers Carrying Essential Elements Other than Nitrogen, Phosphorus and Potash; Uses of Fertilizers Carrying Elements not Accepted as Essential for Plant Growth; Principles Underlying the Use of Fertilizers; Principles Underlying the Purchase of Fertilizers; The Application of Fertilizers and the Influence of Fertilizers on Germination and Seedling Growth. These are followed by a bibliography and author and subject-matter indexes. The author has rendered a distinct service in having made available in textbook form much new information.

Methoden für die Untersuchung des Bodens. II. Teil. By O. LEMMERMANN and L. FRESENIUS. Verlag Chemie, G. m. b. H., Berlin, 1934. Pp. 122, figs. 4.

The first part of *Methoden für die Untersuchung des Bodens* appeared in 1932. It was the intention of the authors, as indicated in the Preface of Part I, to develop a series of treatises devoted to methods of soil investigation. The scope of the work is indicated by the following arrangement of the subject matter: A. The Sampling of Soils; B. The Physical Investigation of Mineral and Organic Soils; C. The Investigation of Mineral Soils; D. The Investigation of Peat and Muck Soils; and E. The Investigation of Forest Soils.

Under topic A, the authors discuss methods of sampling different types of soils. The use of the samples for profile studies, for mapping, and for research on the physical and chemical properties of soils is indicated. In Section B, the principal subjects dealt with are the mechanical analysis of soils, the determination of specific gravity, the determination of the heat of wetting, the determination of vapor absorption, the measurement of soil structure, the determination of the "critical" water relations, air content, and specific porosity. Section C supplies information on the analysis of soils by gravimetric and colorimetric methods. It has to do, likewise, with the ascertaining of the fertilizer requirements of soils and their microbiological investigation. Section D has

to do with the chemical and microbiological investigation of peat and muck soils. Section E deals in particular with the chemical study of various soils. The authors have presented the subject matter in a compact way and have made available to the teacher and research worker valuable reference material.

Electrokinetic phenomena and their application to biology and medicine. By HAROLD A. ABRAMSON, The Chemical Catalog Company, Inc., New York, 1934. Pp. 331, figs. 106, tables 57.

This book is one of the American Chemical Society series of scientific and technical monographs. Its relation to the other books in the series is indicated by the following statement of the editor of the series: "By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development." The purpose of the editors is further indicated by the statement: "Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended."

The author, in his preface, says: "This monograph may find its justification in the attempt to bring together in a more or less harmonious whole, ideas and experiments from remote aspects of physics, chemistry and biology, many of them seemingly unrelated and obscure."

The scope of the monograph is indicated in the titles of the several chapters. They are: Historical; Early Theory and Related Experiments; Methods; Recent Theory and Related Experiments; Proteins and Some Related Compounds; General Effects of Salts on "Inert" Surfaces; Inorganic Surfaces; Organic Surfaces: Gases: Blood Cells, Spermatozoa, Tissues, Etc.; Bacteria, Antibodies, Viruses and Related Systems. There are three appendixes, dealing, respectively, with Notation, Constants and Conversion Factors, and Patent Literature. These are followed by author and subject-matter indexes. The

field of inquiry covered by this monograph is so broad as to make the book of wide interest to research workers in practically every important field. They have been placed under obligation both to the Board of Editors and the author.

Soil Analysis. A Handbook of Physical and Chemical Methods. By C. HAROLD WRIGHT. Thomas Murby & Co., London, 1934. Pp. viii + 236, figs. 6.

The methods of soil analysis developed within recent years have made obsolete many of the older analytical data. A vast mass of work was done with the hydrochloric acid extraction method. Much of this is now valueless. This fact has served to stress the importance of agreement among chemists as to methods employed in soil analytical work. Otherwise, the data obtained by different analysts are not comparable. The author of *Soil Analysis* has brought together the more recent as well as the older information on the technique of soil analytical work. For this reason, the book should be useful to many workers in the field of soil science. The author notes, in the Preface, that "While those engaged in the many branches of applied chemistry can obtain full details of their methods of analysis from laboratory manuals, the pedologist is to a large extent dependent on journals and other publications for the details of the methods of examining the soil." The author says, further: "Great care has been taken to include all the working details of each method. Under each heading is given a description of the method as it was originally described in the publication referred to; any additional information and comments by me are included in foot-notes. Data required in calculating the results are given for easy reference."

The book is made up of three parts, designated, respectively: Physical Methods, General Chemical Methods, and Special Chemical Methods. The appendixes deal with International Atomic Weights, Gravimetric Factors and Their Logarithms, Strengths and Equivalent Values of Standard Solutions. There are also author and subject-matter indexes.

The American Farmer and the Export Market. By AUSTIN A. DOWELL and OSCAR B. JESNESS. The University of Minnesota Press, Minneapolis, Minn. 1934. Pp. vi + 269, figs. 4, tables 15, illus. 2.

The export of agricultural products assumed importance even in our colonial times. The volume of exports gradually increased until we have come to depend on foreign markets for the absorption of large volumes of our agricultural commodities. Cotton and tobacco are notable among the crops depending on foreign markets for an outlet. Very substantial amounts of wheat and wheat products, corn and corn products, and pork and pork products have also played a prominent rôle among our agricultural exports. At the present time, there is much difference of opinion among economists as to the road which we are to follow in planning our agricultural production, particularly from the point of view of the absorption of our crop surpluses by the export markets.

The American Farmer and the Export Market represents a timely and intelligent discussion of a subject important to American agriculture and to the Nation at large. The authors have divided the discussion under the following topics: The Farm Plant, The Home Market, and The Export Market. The following may be quoted from the Introduction: "The depression has also stimulated a vast growth in economic nationalism. One of the ways by which this and other countries have sought to improve the situation of their agriculture and other industries has been through restrictions upon international trade. These measures force us to examine critically what export markets mean to the American farmer and what effect nationalistic policies have upon these outlets."

The book should be found helpful and useful in the classroom and to the student of economics. It should also furnish much food for thought to every intelligent reader. The facts marshalled by the authors are presented clearly and effectively. A considerable amount of tabular matter and a list of references add much to the value of the book.

Reshaping Agriculture. By O. W. WILLCOX. W. W. Norton & Co., Inc., New York, 1934. Pp. 157, figs. 10, tables 8.

More than ordinary interest may be attached to *Reshaping Agriculture* because of the rather fundamental changes that the agriculture of this and of other countries is now facing. The most available areas of free and virgin soils have been occupied. Much of the virgin fertility of the land devoted to the production of wheat, corn, rice, cotton, and other staple crops has been depleted. Erosion, cropping, and overgrazing have taken their toll. Students of soil science, as well as economists and statesmen, are now analyzing the problem of land use and are giving consideration to production levels as a significant factor in the maintenance of economic stability. The author of *Reshaping Agriculture* has presented in a most interesting way the possibilities that lie in intensified production and the limits which may be set to yields per acre. To quote the author: "Agricultural technology may never reach, in all its parts, the full condition of perfection foreseen for it by the agrobiologists: but in so far as it tends in any part to approach the limits set for it by Nature it may exert powerful effects on the political, social and economic stages; some of the effects of agrobiological developments are now very painfully evident. The intelligent citizen, not to mention the professional politico-economists and the social-economists who expect to have a share in planning a new social order (which appears to be overdue) must adjust his standpoint to the potentialities of plant life as these have been revealed by the agrobiologists."

The book is made up of a Foreword by Dr. Alvin Johnson, and of eight chapters, entitled: The Real Technical Basis of Farming; The General Relation between Input and Output in Farming; The Maximum Productivity of Land; The Demonstrable Yielding Power of Crop Plants; The Rising Technical Result of Farming; Abolishing the Weather Hazard in Farming; Social Intervention in Agriculture: and "Implementing the Era of Abundance.

Practical Everyday Chemistry. By H. BENNETT. The Chemical Publishing Company, New York, 1934. Pp. xv + 305.

It is evidently the author's intention to help the man in the street to find a better understanding of chemistry as it touches everyday life. To use his own words: "All your life you may have yearned to dabble and putter with chemicals. Perhaps you have been held back by lack of time, facilities, and knowledge. Shorter working hours have given many a leisure which can well be turned to 'riding' a hobby. What more fascinating hobby is there than chemistry? Chemistry—mysterious, alluring and everchanging. To make it even more interesting, why not apply yourself to the practical chemistry of the many things which you use or see daily. As for a laboratory, the attic, kitchen, basement or garage will answer."

The Introduction to the book consists of an explanation of weights and measures, and the main book consists of nineteen chapters. Chapter I, entitled "Abrasives," consists of a description of cements, glues, lutes, and pastes. The second chapter, "Agriculture and Garden Specialties," deals with animal remedies, fertilizers, insecticides, and weed-killers. The third chapter, entitled "Coatings, Protective and Decorative," has to do with lacquers, paints, varnishes, and stains. In the fourth chapter, "Cosmetics and Drugs," we find a discussion of antiseptics, bleaches, creams, deodorants, disinfectants, hair preparations, lipsticks, lotions, perfumes, pharmaceuticals, powders, and proprietaries. The reader will find similar treatment in the following chapters entitled: "Emulsions"; "Food Products; Beverages and Flavors"; "Inks, Carbon Paper, Crayons, Including Duplicators, Mimeograph and Typewriter Supplies"; "Leathers, Skins, Furs, Etc."; "Lubricants, Oils, Etc."; "Materials of Construction"; "Paper"; "Photography"; "Plating"; "Polishes, Abrasives, Etc."; "Rubber, Plastics, Waxes, Etc."; "Soaps and Cleaners"; "Textiles and Fibers"; "Miscellaneous"; and "Tables." The latter contains a list of trade names and suppliers. There is also a satisfactory index.

Practical Bacteriology. By ANDREW CUNNINGHAM. Oliver and Boyd, Edinburgh and London, 1934. Pp. viii + 203, figs. 26.

This a revised and enlarged second edition of the book. It is offered as a text for students in agriculture. The scope of the work is indicated by the titles of the seven chapters. The first three chapters deal with general bacteriological technique, including the preparation of culture media, the use of the microscope, the staining and microscopic examination of bacteria, and the cultivation and characterization of bacteria, moulds, yeasts, and actinomycetes. The following four chapters deal with bacteriology of milk, dairy products and water supplies, bacteriology of soil and farmyard manure, bacteriology of plant diseases, and bacteriology of animal diseases. The three appendixes contain matter relating to bacteriological tests for graded milk; stains and staining reagents; and indicators, chemical reagents, etc.

Practical Bacteriology will be found useful as a laboratory manual for students

specializing in soils, dairy and animal husbandry, plant pathology, and plant physiology. The author has outlined the subject clearly and has arranged the contents of the book in a manner to be most helpful to laboratory classes in introductory bacteriology.

JACOB G. LIPMAN.

THE SOIL-MOISTURE SYSTEM

G. B. BODMAN AND N. E. EDLEFSEN

University of California

Received for publication February 8, 1934

ERRATA

SOIL SCIENCE, Volume 37

Laws of soil colloidal behavior: XIV. Aging of colloids and base exchange, by A. J. Pugh

P. 403—Title of paper should read "Laws of soil colloidal behavior: *I.* Aging of colloids and base exchange." Sentence 2, paragraph 2 of footnote 1 should be deleted. This paper should not be included in Mattson's series "Laws of soil colloidal behavior."

Volume 38

Laws of soil colloidal behavior: XV. Ionic exchange with hydroxides, by A. J. Pugh

P. 161—Title of paper should read "Laws of soil colloidal behavior: *II.* Ionic exchange with hydroxides." This paper should not be included in Mattson's series "Laws of soil colloidal behavior."

Base exchange studies on the Pennsylvania Jordan field plots, by F. G. Merkle

P. 50—Seventh line from bottom of page, table *I* should read table *II.*

specializing in soils, dairy and animal husbandry, plant pathology, and plant physiology. The author has outlined the subject clearly and has arranged the contents of the book in a manner to be most helpful to laboratory classes in introductory bacteriology.

JACOB G. LIPMAN.

THE SOIL-MOISTURE SYSTEM

G. B. BODMAN AND N. E. EDLEFSEN

University of California

Received for publication February 8, 1934

The soil may be regarded, with respect to soil moisture, as a porous medium consisting of inorganic and organic solid, liquid, and gaseous phases. The volume composition of the soil varies to a greater or lesser extent from time to time. Although this is true in some measure of all phases of the soil mass in the surface layers of cultivated soils, it is particularly true of the relative quantities of the liquid and gaseous phases at all depths from the surface above a permanent water table. The volumes of liquid and gases present in a given soil are complementary to each other and affected by such factors as precipitation, humidity, plant life, and many others characteristic of the soil itself.

THE SOLID FRAMEWORK

The nature of the solid phase can be outlined only briefly. It consists of relatively insoluble and also soluble constituents. The former include various-sized fragments of rock and minerals, plant and animal residues, microorganisms, and secondary products derived from them. The small quantities of soluble and ionizable solids have been produced by chemical and microbiological decomposition of the solid phase. Any colloidal particles which may be present are subject, because of their great specific surface, to certain changes of individual form, relative arrangement, and mobility, induced by variations in moisture content of the soil mass, or by the abundance and nature of the ions upon their surfaces. Such changes are not impressed to an appreciable extent upon the coarser particles of the soil. The insoluble particles of the soil phase in any given part of the soil section possess a certain size distribution, which as far as the inorganic part is concerned, may be measured with moderate success. They provide the soil mass with an abundance of interstitial pores, many of which may be ultra-microscopic in size.

CLAY AND THE MICROSTRUCTURE

It appears probable that, at very low moisture contents, the fine clay of the soil may have entrapped within its crystal lattices some water molecules which are so hindered from ready escape that they exert immeasurably slight vapor pressures at ordinary temperatures. This may also be true of the organic components and to a less extent of the coarser and less completely weathered

inorganic particles. Interplanar spacings have been reported (26, 31) for certain soil colloids, halloysite, and a bentonitic colloid, some of which are in excess of the molecular diameter of water (30). Simon and Schmidt (45) plotted temperature-composition curves for various synthetic ferric-oxides and obtained continuous curves for the region from 300° down to 20°C., which indicated the existence of adsorbed water rather than of any definite hydrates. Van Bemmelen's well-known researches (51) showed that exposure in the atmosphere above concentrated sulfuric acid was insufficient to remove the last traces of water from freshly prepared silica gel. Both colloidal ferric oxide and colloidal silica probably exist as such in many soils, as well as the more complex and definitely crystalline but colloidal aluminosilicates. Ross and Shannon (41) found that a sample of montmorillonite, which had been dried to constant weight at 100°C. lost an additional 9.6 per cent of water upon being further heated to red heat. Puri, Crowther, and Keen (38) obtained a linear increase in loss of weight with increasing temperature on heating a clay subsoil to a series of temperatures between 100° and 200°C., although Coutts' data (15), extending over a wider temperature range, indicate a lack of linearity. Organic matter may be expected to interfere with any interpretation of these curves as to the presence of water of crystallization. It was pointed out by Langmuir (33) that the apparent thickness of adsorbed films on glass surfaces is due to the permeability of the glass itself, the greater portion of the vapor retained by the glass being present within it. Failure to reckon with this possibility may affect to a serious extent calculations aimed at an estimate of the thickness of an adsorbed film on soil particles.

Altogether, there is considerable evidence in support of the idea that even the most minute recesses are accessible to molecules of water vapor.

ADSORPTION AND ESCAPE OF WATER MOLECULES

The relationship existing between the solid and liquid phases may be traced conveniently by a consideration of the conditions occurring because of the action of water vapor as the soil passes from a relatively dry to a relatively wet state. The first few molecules of water which bombard the solid phase will be retained with extreme tenacity. Some, as indicated above, may find their way actually within the lattice itself; the bulk, however, will be adsorbed as a thin layer upon the walls of minute capillary pores. Summaries of the results of adsorption measurements indicate, according to Adam (1), that the ease of adsorption is proportional to the ease of liquefaction of the gas, a fact which has been regarded as pointing, although inconclusively, to condensation of the vapor in the smallest pores by actual liquefaction. This condensation results in a progressive filling of the micropores, if not an actual thickening of the adsorbed surfaces, until finally the very smallest spaces are full. Further additions of water result in a relatively slower change in the configuration of the water surface. In visualizing the wetting process, it makes little difference actually whether it is supposed that all surfaces are first covered

with a mono-molecular layer which is followed by condensation in the capillaries, or whether a layer many molecules in thickness is assumed to be deposited on the surfaces. The result will be the same, the films ultimately coalescing to provide water wedges with characteristic curvatures dependent upon the fineness and arrangement of the soil particles and the amount of moisture. Still further additions of water molecules will gradually fill all

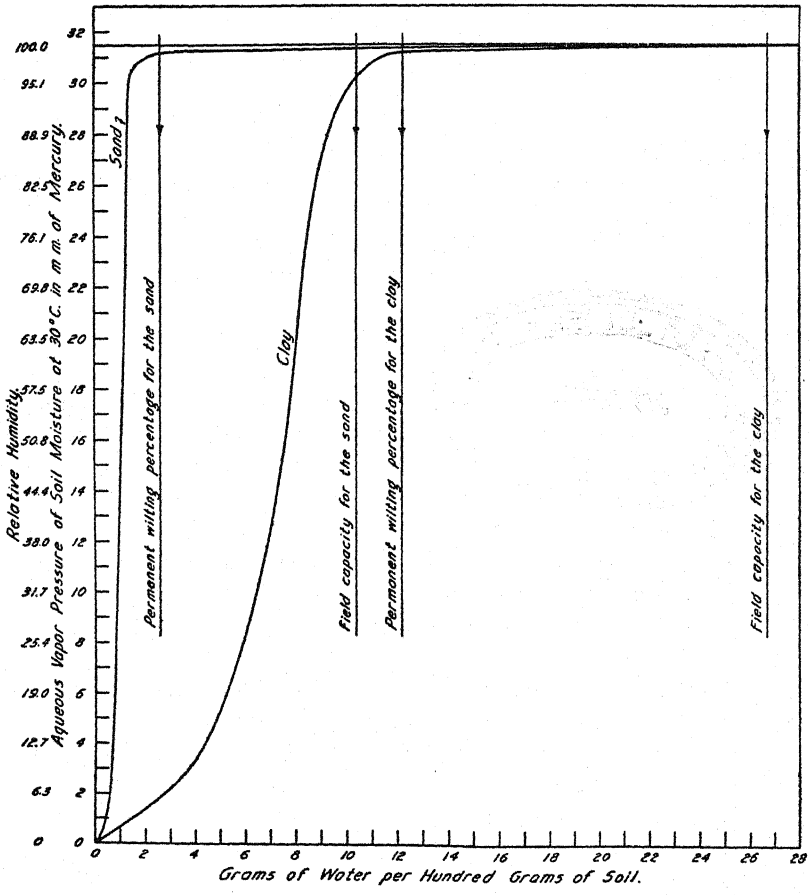


FIG. 1. TYPICAL VAPOR-PRESSURE CURVES FOR SAND AND CLAY, SHOWING WILTING PERCENTAGES AND FIELD CAPACITY

pores until the soil mass is saturated. Although the foregoing presentation assumes the absence of air, its presence will probably have no appreciable effect upon the sequence of events; it may, however, delay equilibrium.

The whole picture may now be viewed, very usefully, from the reverse aspect, with regard to the characteristic escaping tendencies displayed by the water molecules, which will vary in their freedom of movement at the liquid-

gas interface throughout the entire range of soil moisture content. The magnitude of these tendencies to vaporize may be measured conveniently by determining the vapor pressure associated with the soil at a given moistness.

The equilibrium vapor pressure represents, of course, the kinetic energy of the water molecules above the liquid-gas interface. As discussed later, this is dependent upon the relative magnitudes of the forces acting upon the water, the bulk of which is retained in the network of solids. Thomas (48, 49), in this country, and Puri, Crowther, and Keen (38), at Rothamsted, made some of the earliest and most accurate measurements of the vapor pressure of soils. Both dynamic and static methods were used. An improved form of apparatus (18, 19) devised to hasten equilibrium, has recently been developed for vapor pressure measurements by one of the authors.

Because of the importance of the vapor-pressure-moisture-content relationship, the full significance of which is discussed later in this paper, and the rational approach which it provides to the study of both the statics and dynamics of soil moisture, the forms of the vapor pressure curves will be described.

Various workers have found the general form assumed by these curves to be very similar, as indicated in figure 1. Using a coördinate system in which the moisture content of the soil is measured along the axis of abscissas and the vapor pressure, absolute or relative, along the axis of ordinates, and proceeding from the origin, they are found to be concave upwards for varying distances, nearly straight and steepest for some distance on both sides of the region corresponding to about 50 per cent relative humidity, then concave downwards and finally almost linear with a slight upward slope for the uppermost quarter or one-third of their extent. They approach the vapor pressure of pure water as an asymptote with increasing wetness of soil. For any given vapor pressure the finer-textured soils and separated clays of a given kind show higher moisture contents. There is, as might be expected, some connection between the composition of the fine material and its vapor-pressure-moisture relation. This was first pointed out by Anderson and Mattson (7). Determinations made at Berkeley by the static method for certain separated clays showed that a residual lateritic clay having a molecular ratio

$$\frac{SiO_2}{Fe_2O_3 + Al_2O_3} = 1.34$$

behaved very differently from several of the more highly siliceous varieties, the former exerting at much lower moisture contents vapor pressures equal to those shown by the latter at very much higher moisture contents. It is uncertain to what extent these differences, which are less prominent in the region of higher vapor pressures, are due to particle size and to what extent they are caused by characteristic differences in the nature of the surfaces of the two kinds of material.

Most of the measurements that have so far been made of soils or soil sep-

arates at humidities approaching saturation are of questionable exactitude because of the nature of the curve in that region, a very slight increase in vapor pressure corresponding to a great increase in moistness. From the point of view of the plant physiologist, this part of the curve is of greatest interest, since at moisture contents corresponding to these vapor pressures water is readily available to plants (52).

MECHANICAL FORCES ACTING ON SOIL MOISTURE

Some idea of the nature of the mechanical forces acting on the soil moisture may be obtained from the following considerations:

If we examine the horizontal forces acting on the rectangular parallelopiped (fig. 2) of unit cross section perpendicular to the plane of the paper, we note, under equilibrium conditions, that a pressure p acting on the interface EF is in the same direction as the cohesive forces of the remainder of the

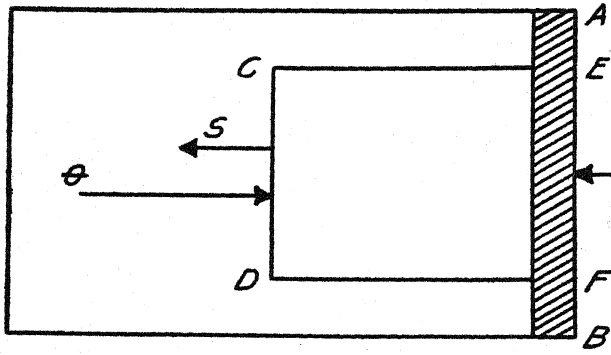


FIG. 2. DIAGRAM OF FORCES ACTING ON ELEMENTAL VOLUME OF WATER
S = cohesive force, θ = kinetic pressure, p = surface pressure acting on the interface EF.

liquid for the liquid in the volume $CDEF$. These two forces are balanced by the kinetic pressure θ of the liquid to the left of the volume $CDEF$ against the face CD so that we may write

$$p = \theta - S \qquad (A)$$

where p is a surface force and for most purposes θ may be regarded as such. On the other hand S is a body force, since it has a field. Other examples of body forces which may act on an element of soil moisture are the gravitational force and the adhesive force, since both possess fields.

Consider the water wedge in figure 3 and assume it small enough so that the effect of gravity on the shape of the air-water interface may be neglected. Let the horizontal plane pass through B'' at a distance below B' equal to the radius of the sphere of attraction of the cohesive forces. The hydrostatic pressures are in equilibrium around the line BB'' under this plane. This is also true of the kinetic pressures around $B''B'$. But above the plane the

molecular attractive forces depend upon the shape of the surface, which is governed by the relative magnitude of the cohesive and adhesive forces. Equation (*A*) holds above this plane as well as below it, but above the plane *S* is not constant with respect to distance from the line $B'B''$.

Another force acting on soil moisture is the attraction of dissolved substances such as salts, which produce an osmotic pressure. In some ways this may be regarded as an adhesive force.

As is pointed out later in this paper, a potential function, consisting of a gravitational potential, an osmotic potential, and a pressure potential, may be set up for soil moisture. The rate of change in any direction of the sum of these with respect to distance produces a conservative force field tending to move moisture in that direction. If any motion takes place, frictional forces are set up tending to resist the motion.

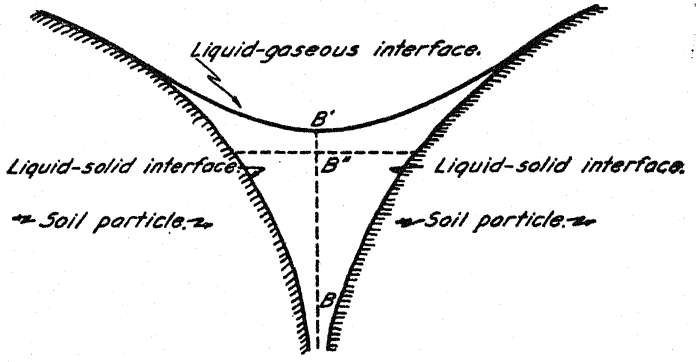


FIG. 3. DIAGRAM OF WATER WEDGE TO ILLUSTRATE FORCES ACTING ON SOIL MOISTURE

As has already been described, the sharp departure at a definite moisture content of a characteristic aqueous vapor pressure curve of soil moisture from the vapor pressure of free water suggests that the adhesive forces begin to predominate at this point. This point has special physiological significance, as has been shown by one of the authors, since it represents the moisture content at which plants wilt.

INTERRELATIONSHIPS OF BASIC FUNCTIONS

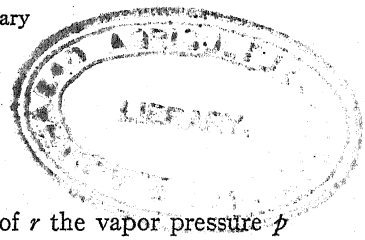
The effective curvature of the water-gas interfaces may be calculated from the vapor pressure exerted by the moisture in the soil. This may be obtained by the consideration of a clean glass capillary tube dipping down into a much larger vessel of pure water or of solution, vessel, tube, and liquid being confined in an evacuated chamber which contains in addition only the water vapor. The meniscus in the capillary is here considered for convenience to be a hemisphere of radius *r*, equal to the radius of the capillary tube. The following equation may be developed, however, without making this assumption. The

relationship between vapor pressure and curvature of liquid surface in such a system is given by the expression

$$\ln \frac{p_0}{p} = \frac{2\sigma}{r} \cdot \frac{M}{\rho RT} \qquad (B)$$

where

p_0 = vapor pressure above the flat surface of water or solution
p = vapor pressure above the curved meniscus in capillary
σ = surface tension of water or solution
M = molecular weight of liquid
r = radius of capillary tube
ρ = density of water or solution
R = gas constant expressed in suitable units
T = absolute temperature



It is accordingly apparent that for small values of r the vapor pressure p approaches zero, whereas with increase in r it approaches the limiting value p_0. This relationship is maintained at least to a first approximation for concentrations of the soil solution such as are usually encountered.

Differences in vapor pressure reported for the same soil at the same moisture content, the magnitudes of which depend upon whether the soil concerned is drying or wetting, have been referred to hysteresis effects. The possibility that true hysteresis may occur will be dealt with in the following discussion.

When the curved meniscus at the water-air interface is again considered, the pressure difference ϕ on opposite sides of the interface is given by the expression

$$\phi = \sigma\left[\frac{1}{r_1} + \frac{1}{r_2}\right] \qquad (C)$$

in which r_1 and r_2 are the two principal radiuses of curvature through the meniscus.

When

$$r_1 = r_2, \phi = \frac{2\sigma}{r} \qquad (D)$$

ϕ is negative when the liquid-vapor interface is concave to the vapor.

Referring now to the enclosed system described above, in which a capillary tube dips into a level water surface, we may express the vapor pressure at any height, h, above the plane surface of water in terms of the height by the exponential equation

$$p = p_0 \cdot e^{-\left[\frac{\rho_0 g h}{p_0}\right]} \qquad (E)$$

in which

e = base of natural logarithms
ρ_0 = vapor density at level water surface
g = gravitational constant

and the remaining symbols have the same meanings as before.

The interrelationships of vapor pressure, curvature of meniscus, pressure difference on opposite sides of the curved meniscus, and height above a plane water surface at which a given vapor pressure and meniscus curvature are in equilibrium, are of greatest significance. They indicate the existence of a connection between a measurable property of the moisture content, namely, its vapor pressure, and an expression of that moistness in terms of energy relations. In other words, by measuring the vapor pressure exerted at a given point in a moist soil, an energy relationship may be calculated and expressed in terms of the work required per unit mass to move water through the soil from some position of reference, where the vapor pressure is also known, to the point in question. Thus, by taking the natural logarithms of both sides of equation (E) we have

$$h = -\frac{p_0}{\rho_0 g} \ln \frac{p}{p_0} \qquad (F)$$

in which h is the distance factor entering the work expression, and refers to the distance under equilibrium conditions from the water surface to the point in the soil mass at which the vapor pressure exerted by the moist soil is p.

A mathematical function called a "potential function" may be introduced conveniently during the consideration of a number of different aspects of the subject of soil moisture. Its use makes possible the development of a dynamical method which aids materially in the study of moisture flow in soils and which removes some of the difficulties in working out a rational soil moisture system. In soils it is known as the capillary potential function, or pressure potential function. It may be thought of as playing a rôle which, in relation to soil moisture flow, is similar to those played by voltage differences in electrical theory and pressure differences in the flow of water in pipes. It is merely a function created by the investigator and is introduced purely as a matter of convenience in analyzing the problem.

The pressure potential may be given the symbol ψ and is defined (21, 27, 39) by the equation

$$\psi = -\int_A^B f ds \qquad (G)$$

or

$$\psi = -\int_A^B \frac{dp'}{\rho} \qquad (H)$$

in which f represents the field force acting per unit mass of moisture, ds is an element of distance along the path, A is an arbitrarily chosen reference point of the zero potential usually taken as a free flat water surface and B is the point in question, p' is the pressure in the fluid, and ρ is the fluid density. This may be stated in words as the work per unit of mass done against the field forces in moving water from the reference point to the point in question.

Under equilibrium conditions and the influence of gravity equation (*G*) takes the form

$$\psi = -\rho gh \qquad (I)$$

Figure 4, which has already appeared elsewhere (19), provides a useful means of examining the interrelationships, at equilibrium, of the internal pressure conditions (*a*) in an osmotic solution, (*b*) in a moist soil, and (*c*) beneath the curved meniscus of a capillary tube. *A* is a chamber with semi-

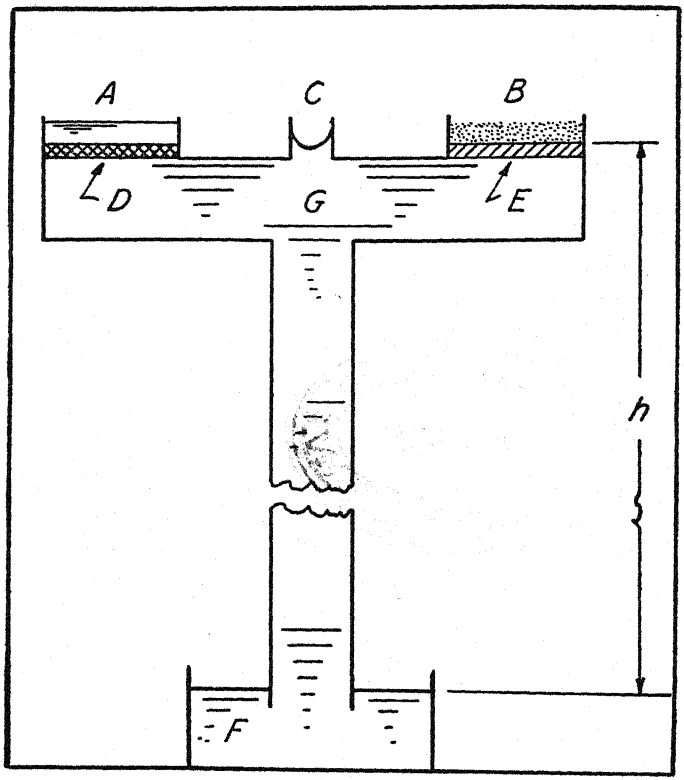


FIG. 4. A SYSTEM FOR DEMONSTRATING THE COLLIGATIVE PROPERTIES OF SOIL MOISTURE

permeable bottom, *D*, containing an osmotic solution; *B* is a chamber with a porous bottom, *E*, containing soil; *C* is the top of a capillary tube of height *h* and of appropriate diameter. *F* is a vessel of water. *G* is filled with water under tension. The system is enclosed in a chamber from which air is evacuated.

The pressure difference across the meniscus in *C* is given by equation (*D*). This difference in pressure, produced by surface tension, is just balanced by the weight of the column of liquid per unit area of height *h*, plus the difference

between the vapor pressure at the free water surface (p_0) and that above the meniscus (p) at C, so that[1]

$$\frac{2\sigma}{r} = \rho gh + (p - p_0) \qquad (J)$$

From which, together with equations (D) and (I), and in view of the fact that ϕ in this case is negative and represents the decrease in pressure due to curvature alone,

$$\psi = \phi + (p - p_0) \qquad (K)$$

From similar reasoning it is evident that the osmotic pressure is given by

$$\pi = \rho\, gh + (p - p_0) \qquad (L)$$

so that ϕ and π are numerically equal, and ψ differs from ϕ by $(p - p_0)$, an amount which is negative and exceedingly small relative to the other magnitudes concerned. It may ordinarily be neglected.

The relationship between vapor pressure (p) and capillary potential (ψ) is shown in figure 5.

In introducing the capillary potential function of soil, it is usually assumed to be single-valued. Under certain conditions, it is possible to conceive of an abrupt change at a given moisture content from a potential characterized by a negative curvature of the surface to a different potential characterized by another negative curvature but at the same moisture content. Under field conditions, however, where the soil has been subjected to forces which have produced a somewhat stable configuration of the soil, it is difficult to see how such a change could occur. It seems very likely that with inter-connected moisture films there could be only one effective curvature of the surface films and hence one potential at a given moisture content. Some investigators (25, 47) have interpreted their results as indicating a phenomenon which is known as hysteresis, which, if it exists at all, means that the potential function may depend on the previous history of the wetting process. Their experiments, however, have been carried on under laboratory conditions, and the results observed may very probably be due to changes in the structure of the soil rather than in the potential function when the structure remains fairly constant.

METHODS OF MEASURING CAPILLARY POTENTIAL FUNCTION

The capillary potential as used in the study of soil moisture was first introduced by Buckingham (13) in 1907. The methods used by him for measuring this function were very slow, and the slowness in arriving at equilibrium made the accuracy uncertain. In the same year, Livingston (36) developed some

[1] The more usual, but approximate, form of this equation is $\frac{2\sigma}{r} = \rho gh$, which is the form ordinarily used in deriving equation (E).

apparatus which he called an "auto-irrigator" which could be used for measuring capillary potential in soils. The relationship between these pieces of work appears to have been overlooked until a considerably later date, when it was pointed out by Gardner and others (21, 27) that the porous clay equipment developed by Livingston could be used for measuring the capillary potential function.

When the soil moisture in contact with a porous cup containing water under controlled pressure comes into equilibrium so far as movement of water is con-

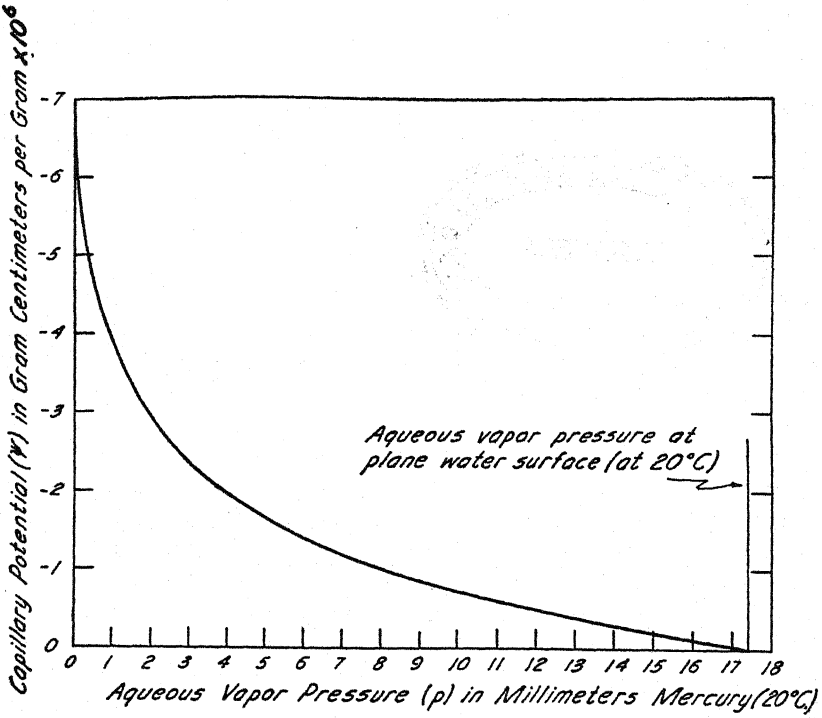


FIG. 5. RELATIONSHIP BETWEEN VAPOR PRESSURE AND CAPILLARY POTENTIAL OF WATER AT 20°C.

cerned, we may state that the potential of the water in the soil is equal to the potential of water inside the cup and the magnitude of the potential has nothing to do with the porous wall separating the two. As has already been pointed out, the potential expressed in the metric system, that is gram-centimeters per gram, is numerically equal to the pressure, since the density of water is unity in this system.

It is observed with such a system of measuring the potential that ordinarily one cannot obtain a potential having a value of greater magnitude than that equivalent to one atmospheric pressure, or 1,034 gm.-cm. per gram, in fact,

unless special precautions are taken, it is difficult to obtain a potential as high as this. On the other hand, it is possible to plot vapor pressure curves over the entire range of soil moisture content from which the capillary potential can be calculated for any given moisture content.

In addition to these two ways of measuring the capillary potential, it might be mentioned that one of the authors has preliminary results on a new method for measuring this function in the field at moisture contents much lower than it is possible to work with by the porous cup method. The method makes use of the high dielectric constant of water in porous media (17). In fact, as shown by the vapor-pressure curves, if one wishes to study the range of moisture as used by plants, it is necessary to be able to measure capillary potential as great as 20,000 gm.-cm. per gram. The necessity of developing a method which will accomplish this is accordingly emphasized.

ARBITRARY SOIL-MOISTURE CONSTANTS

By exposing a soil to some suitably arranged and controlled standard conditions, such for example as exist within a region of definite vapor pressure, or by placing it in some external field of force which will act upon the moisture, it is evident that sooner or later the soil will reach a definite moisture content which represents a condition of actual or approximate equilibrium under the conditions concerned. Provided that the end point represents for these conditions a moisture content having some practical significance for that particular soil, the determination of this moisture content immediately becomes of interest as a method of soil characterization. There have been numerous attempts so to characterize soils physically and to indicate the fact that a sandy soil having a low moisture content may be in equilibrium with a clay soil of higher moisture content. Two methods which have received the greatest amount of attention in this country are those based on the determination of the hygroscopic coefficient and moisture equivalent. The methods of making these determinations have been referred to frequently and are described in papers by Alway and his associates (3, 4), by Briggs and McLane (11), and by Veihmeyer and others (55, 56). They are so well known that they need no further description. Their significance lies in their relationship to soil texture (10), to the amount of unavailable moisture which the soil retains (2, 12, 53), and to that moisture content at which the downward movement of irrigation or rain water is practically negligible (5, 9, 54).

The methods have objectionable features as well as advantages. In any analytical determinations it is highly desirable to have a state of true equilibrium reached. It is difficult in any case to avoid all possibility of the introduction of an arbitrary method of treatment at some point in soil investigations, in which the mere operation of removal from field to laboratory causes more or less serious disturbances in most soils; if equilibrium is not reached an additional arbitrary factor is brought into play. The difficulties of attaining equilibrium and of maintaining the defined conditions of the

determination provide the reasons for the greatest criticism which the hygroscopic coefficient has received (34, 35, 37). The objections were well realized by those who in this country put it to the most extensive and effective use (4). It is evident from figure 1 that wide ranges in moisture content may result at high relative humidities unless the humidity is very closely controlled. The definition of the conditions under which the moisture equivalent is determined emphasize its arbitrary character. Numerous experimental observations confirm this (10, 52). It is nevertheless apparent from an examination of the

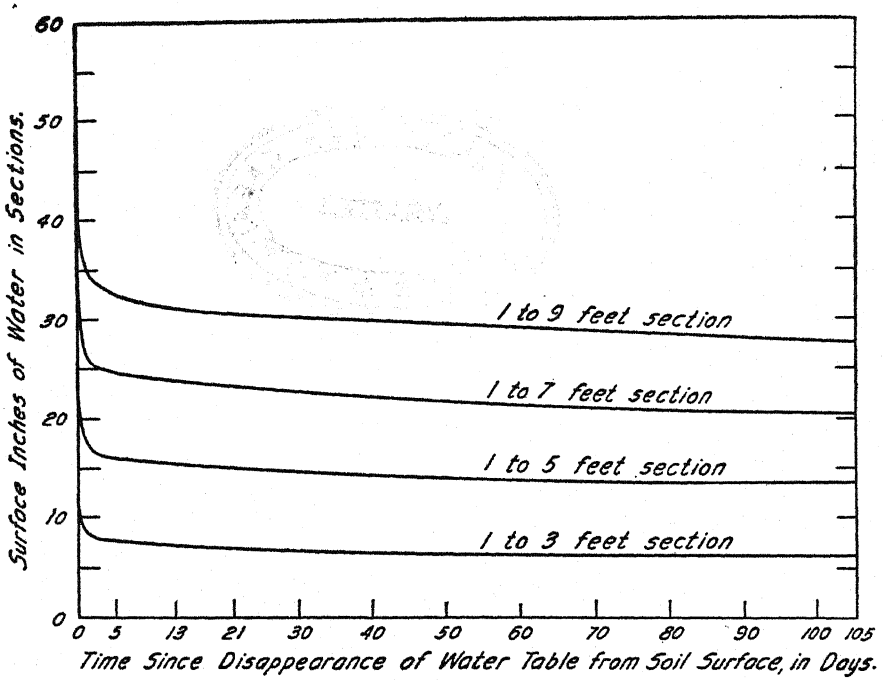


FIG. 6. RELATIONSHIP BETWEEN TIME SINCE DISAPPEARANCE OF WATER TABLE FROM SOIL SURFACE AND MOISTURE CONTENT OF SOIL, EXPRESSED AS SURFACE INCHES

literature that both determinations have shaped the development of a more critical point of view in experiments dealing with the utilization of water and in the interpretation of field moisture data.

Alway and others (6) suggested the use of the hygroscopic coefficient as a reference point in the expression of soil moisture content. Veihmeyer and Hendrickson found that the moisture equivalent is approximately equal numerically to the maximum amount of water which a soil will hold in the root zone and accordingly they have proposed and found useful the term "relative wetness" to describe the ratio of the percentage of moisture in a soil to the moisture equivalent of that soil. They demonstrated with a number of

soils in the field, as did Shaw (43) and Alway and McDole (5) in the laboratory, that movement of moisture is extremely slow after the upper portion of the soil mass has been brought to a moisture content approximately equal to its moisture equivalent. King (32), on the other hand, reported that water continued to drip from columns of sand for $2\frac{1}{2}$ years from the time of their saturation. Data presented in figure 6 (9) indicate the rate of adjustment under field conditions of water in a silt loam soil originally saturated.

FIELD AND LABORATORY OBSERVATIONS ON SOIL MOISTURE MOVEMENT

A comprehensive statement or theory on the subject of soil moisture movement must obviously be consistent with the common practical and experimental observations in the field and laboratory.

It was early noted that in some cases water moved rather rapidly from a wet to a drier soil by capillarity. On the other hand, it has been shown more recently that the extent and rate of such movement may be extremely limited. The rate of rise from deep water tables (44) is of no practical importance. It was observed by many people that this action could be reduced by making an interface in the form of a mulch. Many reports of experiments are available showing the effectiveness of mulches in preventing upward movement of soil moisture. In examining this information, however, it is found that the experiments usually were conducted with some sort of pots to which mulches were applied after irrigation. In some cases, the mulches were made by stirring the surface layer of the wet soil; in others they were applied in the form of dry soil, straw, paper, and so forth. It was definitely shown that under such laboratory conditions the loss by surface evaporation was decreased by the application of a mulch. From these results many recommendations were made to farmers with respect to their cultivation practice. This type of laboratory information was not considered entirely satisfactory, and trials were extended to the field. It was thought by early investigators that their field results showed the value of the mulch in decreasing evaporation, but upon examination of their methods, it is usually found that the amount of decrease in evaporation thought to have been observed might have been explained by the method used in taking the moisture samples. For example, in a certain experiment one field was mulched and another was unmulched. Moisture samples were taken on both fields before mulching, and after a period of time the second samples were taken. In taking the samples on the mulched plot, the dry soil of the mulch was scraped away first, whereas in the unmulched plot, the samples were taken starting at the surface of the ground. This discrepancy in their conclusions was observed by some and corrected in later publications. Many substantiating data indicate that when mulches are applied by implements in the field as soon as the ground is capable of being worked, there is little or no difference between the moisture lost under mulched conditions and that lost when the soil is untouched by a cultivating device. It is found, for example, that approximately half of the soil moisture that will

be lost by evaporation from the surface is already lost before one can get on the field to cultivate it. Practically, there is no significant difference between mulched and unmulched fields in the case of mulches produced by cultivation. It has been demonstrated conclusively, however, that paper and straw mulches applied to the field are effective in preventing evaporation.

It has also been amply demonstrated (2, 14) that, practically, the rate of movement of soil moisture is too slow to supply growing plants with water

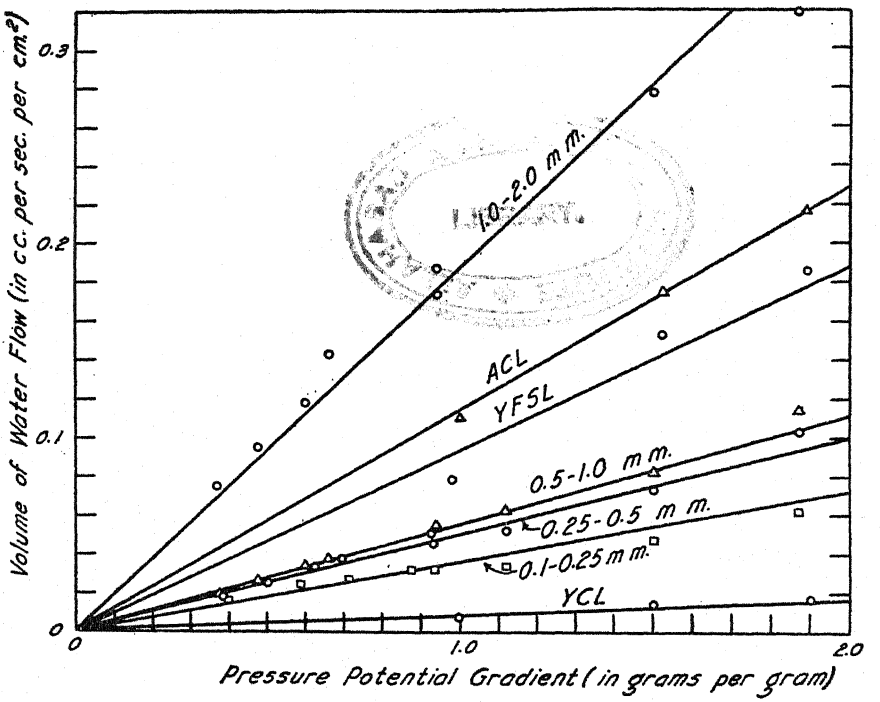


FIG. 7. TRANSMISSION OF WATER THROUGH SATURATED SANDS AND SOILS

The pressure potential gradient may be written in full as gram-centimeters per gram of water per centimeter of column of soil.

Multiply the horizontal scale by 5 for all soils.

Divide the vertical scale by 10 for soil YCL (Yolo clay loam) and YFSL (Yolo fine sandy loam). Divide vertical scale by 50 for soil ACL (Aiken clay loam).

through distances greater than a few inches. In other words, the roots of crops must grow to the water if they are to obtain it.

Considerable effort has been expended on the investigations of the adjustment of moisture distribution in a soil under the action of gravity, starting with a saturated soil. Most of this work has been done in the laboratory, and frequently it is difficult to interpret because of the artificial conditions set up, although many of the experiments do indicate the slowness with which equilibrium is reached. The experience of King, who found that his soil columns continued to drip for at least 2½ years, has already been mentioned.

The subject of the motion of water through soils under saturated conditions has received attention (8, 23, 24, 46, 57, 58), and it has been demonstrated with fair satisfaction that, for most cases at least, the velocity of the water is proportional to the force producing the motion. Unpublished results obtained by one of the authors illustrate the relationship between certain pressure gradient limits as shown in figure 7. It is to be observed that the slope represents the volume of flow per unit potential gradient per unit area.

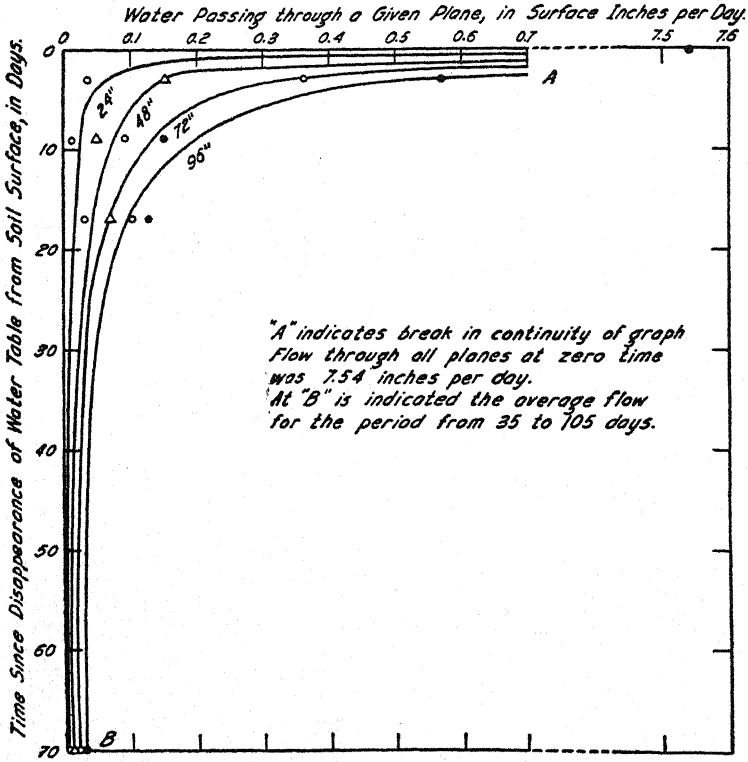


FIG. 8. QUANTITY OF WATER TRANSMITTED THROUGH SOIL PLANES IN SURFACE INCHES PER DAY AS RELATED TO DEPTH AND TIME

This is constant for a given material over the range observed and may be termed the "transmission function."

Field observations on the downward movement of water in soils are of great importance in irrigated regions, and many such experiments have been conducted (9, 28, 42). They involve a study of the motion under saturated conditions as well as the adjustment of the moisture distribution after irrigation water has disappeared from the surface. Results obtained in the field by the authors on the downward motion of water in a silt loam soil, already referred to, are shown in figure 8. The rate of penetration under saturated conditions

was observed by measuring the rate of sinking of the water surface above the soil. The downward motion after the water had disappeared from the surface was obtained by detailed soil moisture sampling at later dates. The plot was covered to prevent losses by evaporation. It is noteworthy that as late as 105 days after irrigation approximately 0.03 inch of water per day passed downward across a plane situated 9 feet below the soil surface.

THE THEORY OF SOIL MOISTURE MOVEMENT IN THE LIQUID PHASE

Progress has been made by several investigators (13, 22, 27, 39, 40, 46) toward working out a satisfactory theory of soil moisture movement. It is recognized that if a quantitative treatment is to be given, the forces and energy relations involved must be taken into account. For this reason, it is found desirable to introduce a capillary potential function, as has been pointed out. This quantity is related to the movement of soil moisture, since its rate of change with respect to distance gives a force acting on the moisture. This force and the force of gravity are the principal forces tending to produce motion of soil moisture under field conditions and account for the motion observed. When one is dealing with the motion of water from the soil into plants and from there into the air, it is convenient to introduce an osmotic potential function. The osmotic potential may also be useful in analyzing soil-moisture conditions when the salt concentration of the soil solution varies with distance. Where bodies move under the action of conservative forces, the resultant of the effective forces is a measure of the acceleration. This is not true when friction is a factor, as in the case of the movement of water in soils, and a velocity is soon reached at which the frictional force becomes equal and opposite to the resultant of the effective forces.

In such slow motion as that of water in soils, there is considerable evidence to justify the assumption that the frictional forces are proportional to the velocity. This may be expressed mathematically by the simple equation

$$V = K F = K \nabla (\psi + \omega + \lambda) \qquad (M)$$

where V represents the mean velocity per unit cross section; K represents the proportionality factor, the magnitude of which depends upon the frictional forces set up by the soil; F represents the driving force per unit mass composed of gradients of the capillary potential, ψ, due to hydrostatic pressure, the gravitational potential, ω, due to the position in the gravitational field, and the osmotic potential, λ, due to an osmotic pressure (34). The factor K may be regarded as a transmission function. Equation (M) simply states that the force acting on soil moisture and, consequently, the velocity are proportional to the greatest space rate of change of the sum of the three potentials and have a direction the same as the direction of the greatest change of this sum. Slichter obtained a solution for this differential equation for the case of flow through saturated soils. Gardner and Widtsoe have made a careful study of

it as applied to unsaturated soils and have shown that the equation takes specific forms when certain boundary conditions exist.

In their treatment, they assumed K to be proportional to moisture content and ψ to be a linear function of the reciprocal of the moisture density. They treated three special cases and obtained a solution for the case of the downward movement of a column of water in a soil with no surface energy developed at either top or bottom. This case is nearly realized during the time a field is covered with irrigation water to a very shallow depth.

They also analyzed the case where the water was removed from the surface and an equilibrium distribution of moisture had been obtained such that the gradient of the capillary potential produced a force equal and opposite to g, which is the gradient of the gravitational potential, ω. The osmotic potential was presumably assumed to be constant. They also obtained a solution for the equation when only horizontal flow was experienced, and presented experimental results obtained in the laboratory which indicated that their solutions fitted the facts reasonably well.

Richards recently has gone further and has investigated for several types of soils the manner in which K depends upon ψ.

MOVEMENT OF WATER IN THE VAPOR PHASE

Water vapor may move through the soil by diffusion at constant temperatures and static air conditions. This motion is extremely slow, as pointed out by Ewing and Linford (20, 35), who have made contributions which are valuable in forming a satisfactory physical basis for describing the motion of vapor through soils, and it is therefore of little practical importance. This state of extremely slow motion probably has been mistaken for a state of equilibrium in some cases. This may be far from the truth and may lead to errors of considerable importance. The diffusion is more rapid if there is a temperature gradient. By far the larger amount of vapor movement in soils is through the convection currents of the soil air which carry water vapor in varying amounts. The "breathing" of soil due to changes in barometric pressure may cause movement either into or out of the soil, but the quantity of moisture moved by this means is probably small.

Much information is available on evaporation from soils under laboratory and field conditions, but the movement of vapor through them has received but little attention.

REFERENCES

(1) ADAM, NEIL KENSINGTON 1930 The Physics and Chemistry of Surfaces. Oxford.
(2) ALWAY, F. J. 1913 Studies on the relation of the non-available water of the soil to the hygroscopic coefficient. Univ. Nebr. Res. Bul. 3.
(3) ALWAY, F. J. 1917 Some notes on the direct determination of the hygroscopic coefficient. *Jour. Agr. Res.* 11: 147–166.
(4) ALWAY, F. J., AND CLARK, V. L. 1916 Use of two indirect methods for the determination of the hygroscopic coefficients of soils. *Jour. Agr. Res.* 7: 345–359.
(5) ALWAY, F. J., AND MCDOLE, G. R. 1917 Relation of the water retaining capacity of a soil to its hygroscopic coefficient. *Jour. Agr. Res.* 9: 27–71.

(6) ALWAY, F. J., MCDOLE, G. R., AND TRUMBULL, R. S. 1918 Interpretation of field observations on the moistness of the subsoil. *Jour. Amer. Soc. Agron.* 10: 265–278.

(7) ANDERSON, M. S., AND MATTSON, SANTE 1926 Properties of the colloidal soil material. U. S. Dept. Agr. Dept. Bul. 1452.

(8) BLANCK, E. 1930 Handbuch der Bodenlehre VI. Die Physikalische Beschaffenheit des Bodens. Berlin.

(9) BODMAN, G. B., AND EDLEFSEN, N. E. 1933 *Science* (n. s.) 78 (No. 2025): 355. (See Abstracts of papers presented at the meeting of the Western Society of Soil Science at Salt Lake City, Utah, June, 1933, for abstract.)

(10) BODMAN, G. B., AND MAHMUD, A. J. 1932 The use of the moisture equivalent in the textural classification of soils. *Soil Sci.* 33: 363–374.

(11) BRIGGS, L. J., AND MCLANE, J. W. 1907 The moisture equivalent of soils. U. S. Dept. Agr. Bur. Soils Bul. 45.

(12) BRIGGS, L. J., AND SHANTZ, H. L. 1912 The wilting coefficient for different plants and its indirect determination. U. S. Dept. Agr. Bur. Plant Indus. Bul. 230.

(13) BUCKINGHAM, E. 1907 Studies on the movement of soil moisture. U. S. Dept. Agr. Bur. Soils Bul. 38.

(14) CONRAD, J. P., AND VEIHMEYER, F. J. 1929 Root development and soil moisture. *Hilgardia* 4: 113–134.

(15) COUTTS, J. R. H. 1932 Single value soil constants: A study of the significance of certain soil constants VI. *Jour. Agr. Sci.* 22: 200–202.

(16) EDLEFSEN, N. E. 1932 Forces acting on soil moisture in relation to other fundamental functions. *Trans. Amer. Geophysical Union 13th Ann. Meeting*, Washington, D. C., April, 1932: 328–330.

(17) EDLEFSEN, N. E. 1933 A review of results of dielectric methods of measuring moisture present in materials. *Agr. Engin.* 14: 243–244.

(18) EDLEFSEN, N. E. 1933 A glass wool cell for measuring aqueous vapor pressure. *Rev. Sci. Inst.* 4: 345–346.

(19) EDLEFSEN, N. E. 1934 A new method of measuring the aqueous vapor pressure of soils. *Soil Sci.* 38: 29–35.

(20) EWING, SCOTT 1922 The movement of saturated water vapor through quartz flour. *Soil Sci.* 13: 57–61.

(21) GARDNER, W., ISRAELSEN, O. W., EDLEFSEN, N. E., AND CLYDE, H. S. 1922 The capillary potential function and its relation to irrigation practice. *Phys. Rev.* 20: 196.

(22) GARDNER, W., AND WIDTSOE, J. A. 1921 The movement of soil moisture. *Soil Sci.* 11: 215–232.

(23) GREEN, W. H., AND AMPT, G. A. 1911 Studies on soil physics (pt. 1) The flow of air and water through soils. *Jour. Agr. Sci.* 4: 1–24.

(24) GREEN, W. H., AND AMPT, G. A. 1912 Studies on soil physics (pt. 2) The permeability of an ideal soil to air and water. *Jour. Agr. Sci.* 5: 1–26.

(25) HAINES, W. B. 1930 Studies in physical properties of soils: V. The hysteresis effect in capillary properties and the modes of distribution associated therewith. *Jour. Agr. Sci.* 20: 97–116.

(26) HENDRICKS, S. B., AND FRY, W. H. 1930 The results of X-ray and microscopic examinations of soil colloids. *Soil Sci.* 29: 457–479.

(27) ISRAELSEN, O. W. 1927 The application of hydrodynamics to irrigation and drainage problems. *Hilgardia* 2: 479–528.

(28) ISRAELSEN, O. W., AND WEST, F. L. 1922 Water holding capacity of irrigated soils. Utah Agr. Exp. Sta. Bul. 183.

(29) JOSEPH, A. F., AND MARTIN, F. J. 1923 The moisture equivalent of heavy soils. *Jour. Agr. Sci.* 13: 49–59.

(30) KAYE, G. W. C., AND LABY, T. H. 1926 Tables of Physical and Chemical Constants, Ed. 5. Longmans, Green and Co., London.

(31) KELLEY, W. P., DORE, W. H., AND BROWN, S. M. 1931 The nature of the base exchange material of bentonite, soils and zeolites, as revealed by chemical investigation and X-ray analysis. *Soil Sci.* 31: 25–56.
(32) KING, F. H. 1907 Physics of Agriculture. Madison, Wisc.
(33) LANGMUIR, I. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *Jour. Amer. Chem. Soc.* 40: 1361–1403.
(34) LINFORD, L. B. 1926 The relation of light to soil moisture phenomena. *Soil Sci.* 22: 233–252.
(35) LINFORD, LEON B. 1929 Soil moisture phenomena in a saturated atmosphere. *Soil Sci.* 29: 217–237.
(36) LIVINGSTON, B. E. 1908 A method for controlling plant moisture. *Plant World* 11: 39–40.
(37) PURI, A. N. 1925 A critical study of the hygroscopic coefficient of soil. *Jour. Agr. Sci.* 15: 272–283.
(38) PURI, A. N., CROWTHER, E. M., AND KEEN, B. A. 1925 The relation between the vapour pressure and water content of soils. *Jour. Agr. Sci.* 15: 68–88.
(39) RICHARDS, L. A. 1928 The usefulness of capillary potential to soil moisture and plant investigators. *Jour. Agr. Res.* 37: 719–742.
(40) RICHARDS, L. A. 1931 Capillary conduction of liquids through porous mediums. *Physics* 1: 318–333.
(41) ROSS, C. S., AND SHANNON, E. V. 1926 The minerals of bentonite and related clays and their physical properties. *Jour. Amer. Ceramic Soc.* 9: 77–96.
(42) SCOFIELD, CARL S., AND WRIGHT, COULSEN C. 1928 The water relations of Yakima Valley soil. *Jour. Agr. Res.* 37: 65–86.
(43) SHAW, C. F. 1927 The normal moisture capacity of soils. *Soil Sci.* 23: 303–317.
(44) SHAW, C. F., AND SMITH, A. 1927 Maximum height of capillary rise starting with soil at capillary saturation. *Hilgardia* 2: 399–409.
(45) SIMON, A., AND SCHMIDT, TH. 1925 Ueber Eisenhydrate und Eisenoxyde (in Zsigmondy-Festschrift). *Kolloid Ztschr.* (sup.) 36: 65–80.
(46) SLICHTER, C. S. 1898 Theoretical investigations of the motion of ground water. *U. S. Geol. Survey 19th Ann. Rept.* pt. 2: 301–384.
(47) SMITH, O. W., FOOTE, PAUL D., AND BUSANG, P. F. 1931 Capillary rise in sands of uniform spherical grains. *Phys. Rev.* 37: 1015–1016.
(48) THOMAS, MOYER D. 1921 Aqueous vapor pressure of soils. *Soil Sci.* 9: 409–434.
(49) THOMAS, MOYER D. 1924 Aqueous vapor pressure of soils: II. Studies in dry soils. *Soil Sci.* 17: 1–18.
(50) THOMAS, M. D., AND HARRIS, K. 1926 The moisture equivalent of soils. *Soil Sci.* 21: 411–424.
(51) VAN BEMMELEN, J. M. 1910 Die Absorption. Dresden.
(52) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1927 Soil moisture conditions in relation to plant growth. *Plant Physiol.* 2: 71–82.
(53) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1928 Soil moisture at permanent wilting of plants. *Plant Physiol.* 3: 1–2.
(54) VEIHMEYER, F. J., AND HENDRICKSON, A. H. 1931 The moisture equivalent as a measure of field capacity of soil. *Soil Sci.* 32: 181–193.
(55) VEIHMEYER, F. J., ISRAELSEN, O. W., AND CONRAD, J. P. 1924 The moisture equivalent as influenced by the amount of soil used in its determination. Calif. Agr. Exp. Sta. Tech. Paper 16.
(56) VEIHMEYER, F. J., OSKERKOWSKY, J., AND TESTER, K. B. 1927 Some factors affecting the moisture equivalent of soils. *Proc. First Internatl. Cong. Soil Sci.* 1: 1–23.
(57) WYCKOFF, R. D., BOTSET, H. G., AND MUSKAT, M. 1932 Flow of liquids through porous media under the action of gravity. *Physics* 3: 90–113.

THE CUNNINGHAMELLA PLAQUE METHOD OF MEASURING AVAILABLE PHOSPHORUS IN SOIL[1]

A. MEHLICH, E. B. FRED AND E. TRUOG[2]

University of Wisconsin

Received for publication December 26, 1933

Biological methods of measuring the available plant food of soils, especially phosphates, have been the object of numerous investigations, and the literature pertaining to this subject is so extensive and so well known that citations to it are largely omitted in this paper. The idea of using microörganisms to determine the availability of the plant nutrients of soils appears both sound and practical. Unfortunately, most of the methods proposed for this purpose either are complicated and time consuming or do not give reliable results. This investigation represents an attempt to devise a simple and improved biological test for determining the phosphate needs of soils.

EXPERIMENTAL

A test which involves the direct use of soil instead of liquid cultures is desirable from the standpoint of simplicity. The use of certain species of molds is desirable from the standpoint of rapidity of growth, resistance to variations in reaction, and ease of observation of results. Beginning, therefore, with the plaque procedure, numerous experiments were conducted in which various molds were seeded on soil plaques. Some 15 species of molds were grown on soil plaques; namely, (*a*) *Aspergillus niger;* (*b*) *A. oryzae;* (*c*) *A. terreus;* (*d*) *A. sydowi;* (*e*) *A. parasiticus;* (*f*) *A. carbonarius;* (*g*) *A. nidulans;* (*h*) *A. wentii;* (*i*) *Penicillium purpurogenum;* (*j*) *P. islandicum;* (*k*) *P. aurantiobrunneum;* (*l*) *Hormodendrum* sp.; (*m*) *Rhizopus nigricans;* (*n*) *Mucor genevensis;* and (*o*) *Cunninghamella* sp. Both lateral and vertical growth was observed with cultures of *Rh. nigricans* and *Cunninghamella* sp. As a result of these tests, *Cunninghamella* sp. was chosen because of its quick response to the supply of available phosphate. This organism belongs to the same

[1] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[2] The authors are indebted to Prof. E. A. Mitscherlich of the University of Königsberg, Germany, for supplying the samples of soil and his results given in table 8; to Prof. R. D. Hockensmith of the Colorado Experiment Station and to Prof. A. H. Post of the Montana Experiment Station for supplying the samples and field results given in table 7; to the Experiment Stations of Ohio, Michigan, New York, Massachusetts, Alabama, Virginia, and West Virginia for supplying many of the samples of soil and field results given in table 6; and to Dr. H. C. Greene of this laboratory and also to Dr. A. F. Blakeslee of Cold Spring Harbor, for the cultures of fungi.

general group of fungi as the common gray bread mold, *Rhizopus*. It grows very rapidly, producing a tufted and raised mat of grayish hyphae which soon cover the surface of the culture medium.

Cultures of four species of *Cunninghamella* were grown on 10 soils containing varying amounts of available phosphate. The results of these preliminary tests indicated that the growth of this mold is greatly influenced by the amount of available phosphorus. Although the individual species were not exactly alike, their plus and minus strains showed good agreement. From a number of tests in various soils it was concluded that *C. elegans* and *C. blakesleeana* are best suited for the test, followed by *C. echinulata*, and finally *C. berthollotiae*, which is least suited, since its hyphal growth is less rapid and less dense. In subsequent tests, the minus strains of *C. elegans* and *C. blakesleeana* were used. The stock cultures have been carried on the following medium: malt extract, 25 gm.; agar, 20 gm.; and water, 1,000 cc. For comparative purposes, reserve cultures were carried on sterilized soil. No difference has been noted in the cultures carried on malt agar and on soil.

It was found that *Cunninghamella* is able to use nitrogen in the form of ammonia as well as in the form of nitrate. Ammonium nitrate was found to be especially suited, since both the cation and anion are utilized as sources of nitrogen, and, therefore, this salt does not bring about any great change in reaction. In order to induce the maximum growth, organic nitrogen, in a form like peptone, should be furnished in small amounts, as well as adequate amounts of inorganic salts customarily used in synthetic culture media.

Details of the test

The amount of nutrient solution required in the preparation of the plaque depends upon the kind of soil; usually the best results are obtained if the soil is just saturated. A film of liquid should never appear on the smoothed surface, as this will introduce considerable error, especially in soils high in available phosphates. Instead of aerial hyphae, mycelial growth of a type which does not allow accurate measurement will appear. In order to induce a uniform growth, a very small drop of a rich suspension of spores should be added to the center of the plaque. This method of inoculating the soil plaque prevents undue spreading of the fungous spores. Other methods of seeding the spores were tried, *e.g.*, use of a viscous spore suspension in starch solution or vegetable oil, and also very thin pieces of filter paper about 3 mm. in diameter dipped in a rich spore suspension.

It is important to maintain standard conditions of temperature and humidity during incubation. The optimum temperature for *Cunninghamella* is about 28° to 29°C., although good growth is obtained at temperatures of 27° to 30°C. Temperature variations influence the growth of the mold, and, wherever accurate results are desired, incubation should be at 28° to 29°C. The time of incubation should be 48 to 50 hours, although the growth is frequently completed at 42 hours.

Preparation of soil samples. The samples should be air-dried or dried in an oven at a temperature not exceeding 50°C. The soil is then passed through a 20-mesh sieve and thoroughly mixed. The reaction is determined, and if the pH is lower than 7.5 the sample may be used directly for the test as described later in this paper. Soils with a pH greater than pH 7.5 should be

TABLE 1

Amounts of citric acid required to neutralize various amounts of $CaCO_3$ in soils

AMOUNTS OF $CaCO_3$ IN SOIL	CITRIC ACID NEEDED FOR NEUTRALIZATION OF 50 GM. OF SOIL		
	Weight of crystals	10 per cent citric acid solution	50 per cent citric acid solution
per cent	*gm.*	*cc.*	*cc.*
0.25	0.16	1.60	
0.50	0.32	3.20	
0.75	0.48	4.80	
1.00	0.64	6.40	
1.25	0.80	8.00	
1.50	0.96	9.60	
1.75	1.12	11.20	
2.00	1.28	12.80	
2.50	1.60	16.00	
3.00	1.92	19.20	
3.50	2.24	22.40	
4.00	2.56	25.60	5.12
4.50	2.88	28.80	5.76
5.00	3.20	32.00	6.40
6.00	3.84	38.40	7.60
7.00	4.48	44.80	9.00
8.00	5.12	51.20	10.20
9.00	5.76	57.60	11.60
10.00	6.40	64.00	12.80
11.00	7.04		14.00
12.00	7.69		15.40
13.00	8.32		16.60
14.00	8.96		18.00
15.00	9.60		19.20
16.00	10.24		20.60
17.00	10.88		21.80
18.00	11.52		23.00
19.00	12.16		24.40
20.00	12.80		25.60

adjusted to pH 6.8 to 7.5. A satisfactory procedure for doing this is to determine the approximate $CaCO_3$ content by means of a simple method previously described (4). The required amount of citric acid as given in table 1 is then added.

Preparation of nutrient solution. After a number of different nutrient

solutions had been tested, one prepared as next described was adopted. A stock solution of the following inorganic salts is first prepared:

KCl	20.0 gm.
$MgSO_4 \cdot 7H_2O$	10.0 gm.
$FeSO_4 \cdot 7H_2O$	0.2 gm.
$ZnSO_4 \cdot 7H_2O$	0.2 gm.
Distilled water	100.0 cc.

This stock solution of salts may be kept indefinitely. To avoid decomposition, the final diluted nutrient solution should be made up fresh at least every 2 days, as follows:

Glucose (or cerelose)	25.0 gm.
NH_4NO_3	2.5 gm.
Peptone	0.5 gm.
Stock solution of inorganic salts	5.0 cc.
Phosphorus-free water	1,000.00 cc.

Procedure. About 50 gm. of the soil is placed in one-half of a large Petri dish or other convenient glass container and 10 to 15 cc. nutrient solution added, or just enough for saturation but avoiding an excess as previously explained. After being thoroughly mixed, the soil is transferred to duplicate small Petri dishes (50 mm. dia. by 10 mm. high), and soil plaques are prepared, the surface being smoothed by means of a spatula. The duplicate samples are placed in a pan or dish, the bottom of which is covered with well-moistened blotting paper. By means of a wire loop (3 mm. in dia.) a very small drop of a rich spore suspension of *Cunninghamella* is placed in the center of the soil plaque. In order to make these drops uniformly small, the loaded wire loop is first touched to a clean glass surface to remove any excess of the suspension. The spore suspension is prepared by adding 2 cc. of the nutrient solution to a test tube culture of the fungus grown on malt extract agar. The age of this slant culture should be at least 1 week and not more than 4 weeks. The dish containing the soil plaques is covered with a glass plate, which is removed only for inoculation and observation. To provide for aeration, a strip of paper or wood should be placed between the glass cover and the dish.

The cultures are incubated at 28° to 29°C. for 48 to 50 hours, after which the growth is determined by measuring the diameter of the fungous colony. In rare instances the natural fungous flora of the soil will suppress the growth of *Cunninghamella*. This is avoided when a new sample of soil is taken and heated at 40°C. for several days.

Plate 1 shows the marked response of *Cunninghamella* to the addition of increasing amounts of phosphorus, and the meager growth of the fungus on soils containing small amounts of available phosphorus and abundant growth on soils with good supply of available phosphorus.

Interpretation of results. Tests made with soils of known crop response to phosphorus fertilization suggest the following approximate values of lateral

fungous growth in relation to the requirements of phosphate fertilizer: great need is indicated by a growth less than 10 mm. in diameter; moderate need by a growth between 11 to 15 mm. in diameter; slight need by a growth between 16 and 21 mm. in diameter; and no need by a growth above 22 mm. in diameter. These values will vary somewhat, depending on kind of crops involved and species of *Cunninghamella* used for the test.

Expression of results in p.p.m. of phosphorus

The desirability of expressing the results of the test in terms of pounds per acre or p.p.m. of available phosphorus in the soil is evident. An attempt was made to do this on the basis of the phosphorus absorbed from the soil by the fungus and found by analysis of the tissue. Unfortunately, great difficulty was experienced in separating the hyphae from the soil, and this attempt was thus abandoned.

In estimating the amount of growth, it has been found that for practical purposes it is not necessary to measure the vertical growth, but simply the diameter of the fungous colony. This lateral spreading indicates the relationship of growth to amount of available phosphorus present, and was, therefore, utilized in constructing the growth curves of Mitscherlich (5, 10) for 10 different types of soil.

To each of the 10 different types of soil increasing amounts of phosphorus were added, and then the growth of *Cunninghamella* under these treatments was measured and the effect factor calculated from the relationship:

$$c = \frac{\log (A - y_1) - \log (A - y_2)}{X_2 - X_1},$$

where $\log A$ is the maximum growth, y_1, y_2, etc., are the growths obtained when X_1, X_2, etc., amounts of phosphorus are added. The values of the effect factor (c), as shown for each soil in table 2, are expressed as phosphorus in milligrams per 100 gm. of soil. The value for c varies only from 0.150 to 0.172, and justifies its use, therefore, in calculating the amount of phosphorus in the soil from the relationship:

$$b = \frac{\log A - \log (A - y_0)}{c},$$

where y_0 is the growth obtained without the addition of phosphorus. When the maximum growth and the effect factor are known, the amount of available phosphorus in any other soil can be calculated.

By constructing an average curve from these data such as is given in figure 1, the effect-factor c can be eliminated and the amount of available phosphorus present in any soil may be obtained by simple interpolation on this curve.

It is recognized that the results obtained by the foregoing procedure are influenced to some extent by the phosphate-fixing power of the soils, causing

AMOUNT OF PHOSPHORUS ADDED TO SOILS	DIAMETER OF LATERAL GROWTH ON DIFFERENT SOIL TYPES									
	1	2	3	4	5	6	7	8	9	10
	Marshall silt loam	Miami silt loam	Carrington silt loam	Fox silt loam	Miami silt loam	Coloma sandy loam	Dodgeville silt loam	Plainfield sand	Knox silt loam	Waukesha sandy loam
p.p.m.	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*
0	4	5	6	7	8	8	10	10	12	11
10	10	11	13	11	16	16	16	20	16	20
20	20	22	22	19	27	22	24	26	27	25
30	26	28	29	27	33	27	30	32	34	30
40	32	34	34	33	38	32	35	35	41	34
50	38	39	38	38	41	35	39	38	45	36
60	41	43	41	41	44	39	43	41	47	38
70	44	45	43	44	45	42	45	43	50	39
80	45	47	45	46	46	44	47	44	51	40
90	47	49	47	48	48	46	50	46	53	42
100	48	50	48	48	48	46	50	47	53	42
b*	2.4	2.9	3.6	4.2	5.0	5.2	6.1	6.6	7.0	8.5
c†	.158	.159	.155	.166	.172	.169	.151	.159	.155	.150

*b = p.p.m. of available phosphorus in soils as obtained from the relationship:

$$b = \frac{\log A - \log (A - y_0)}{c}$$

†c = the average effect-factor for each soil.

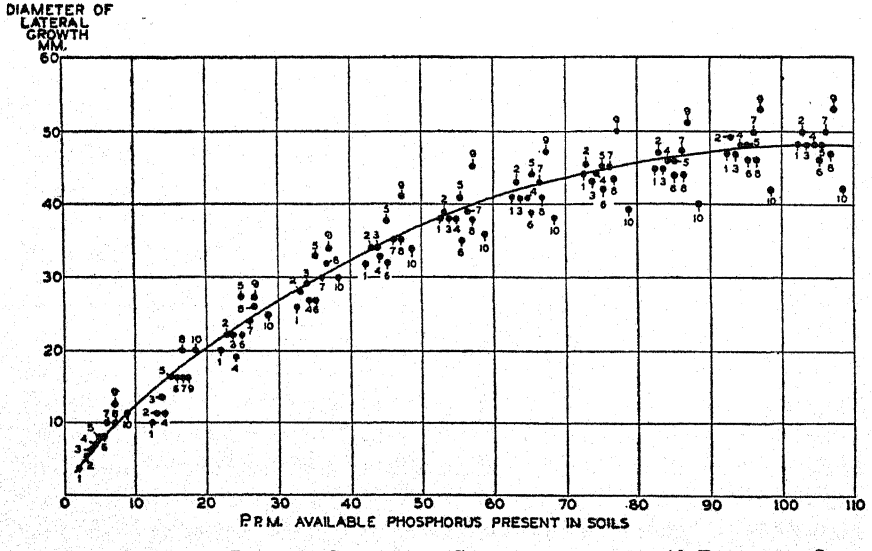


FIG. 1. RELATION OF LATERAL GROWTH OF CUNNINGHAMELLA ON 10 DIFFERENT SOILS BEFORE AND AFTER THE ADDITION OF 10 INCREMENTS OF AVAILABLE PHOSPHORUS

In the series 0 to 10 p.p.m. available phosphorus, the soils contained only their natural supply, which varied from 2.4 to 8.5 p.p.m., calculated according to the Mitscherlich formula. In succeeding series, each soil received increasing amounts (10, 20, 30, etc., p.p.m.), and is represented by dots similarly numbered throughout.

some of the applied phosphorus to become difficultly available. None of these soils, however, have high phosphate-fixing powers and hence this influence has probably not been serious.

Relation of soil reaction and salts to results

In the *Cunninghamella* method, as ordinarily carried out, only small amounts of a nearly neutral nutrient solution are added, and, therefore, the soil reaction undergoes very little change. Increasing amounts of lime may be added to a

TABLE 3

Influence of reaction on the growth of Cunninghamella *on unphosphated and phosphated soils*

REACTION OF SOIL AFTER ADDITION OF LIME	DIAMETER OF LATERAL GROWTH OF CUNNINGHAMELLA	
	No phosphorus added	80 p.p.m. of phosphorus added
pH	*mm.*	*mm.*
4.3	10	42
5.8	10	38
6.5	12	43
7.3	11	40
7.6	5	18
7.9	6	20

TABLE 4

The growth of C. elegans *and* C. echinulata *on soil to which different forms of phosphate were added at the rate of 200 pounds per acre*

CULTURE	DIAMETER OF GROWTH WITH DIFFERENT PHOSPHATES									
	$CaH_4(PO_4)_2 \cdot H_2O$	$CaHPO_4 \cdot 2H_2O$	$Ca_3(PO_4)_2$	$Mg_3(PO_4)_2 \cdot 4H_2O$	$MgNH_4PO_4 \cdot 6H_2O$	$AlPO_4$	$FePO_4 \cdot 4H_2O$	Rock phosphate	$Fe_3(PO_4)_2$	$(NH_4)_2HPO_4$
	mm.	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*	*mm.*
C. elegans	50	43	30	44	40	20	22	15	14	48
C. echinulata	48	42	32	48	41	23	26	18	16	50

soil until it reaches a pH 7.4 to 7.5 without much influence on the growth of *Cunninghamella*. Above a pH 7.5 the effect is quite different, the growth being greatly retarded because of a decreased solubility of the phosphate. Data regarding this matter are given in table 3. These observations agree with the findings of other investigators (1, 2, 3) regarding the decreased availability of phosphate when an excess of calcium carbonate is present. *Cunninghamella* will grow over a wide range of reactions, pH 3.2 to 8.6, and apparently is not easily influenced directly by acid or alkali but is very sensitive to a lowering in the solubility of the phosphates. That this fungus resembles closely the higher plants in respect to the use of phosphorus from various sources, is clearly evident from the data of table 4.

Tests (data not presented) showed that additions of increasing amounts of Mg, Na, Fe, and Zn sulfates, as well as potassium chloride, do not have any marked influence on the growth of *Cunninghamella*.

Comparison of results with other methods

For a comparison of results with other methods, 10 soils containing varying amounts of available phosphorus were selected. These soils were tested with the three biological methods: the *A. niger* method of Niklas (6, 7, 8); the Simakova-Bovschik method (9); the *Cunninghamella* method, and also the chemical method of Truog (11). The results are given in table 5 and show a

TABLE 5

A comparison of the Cunninghamella *method with various other methods of measuring the available phosphate of soils*

SOIL NUMBER	CUNNINGHAMELLA METHOD		SIMAKOVA-BOVSCHIK A. NIGER METHOD		NIKLAS A. NIGER METHOD		TRUOG CHEMICAL METHOD	FIELD TEST
	Diameter of lateral growth	Amount of available phosphorus by curve interpolation	Weight of mycelium from two cultures	Amount of available phosphorus by analysis of mycelium	Weight of mycelium from three cultures	Amount of available phosphorus by analysis of mycelium	Amount of available phosphorus	Increase per acre alfalfa hay due to phosphate fertilization
	mm.	*p.p.m.*	*mgm.*	*p.p.m.*	*mgm.*	*p.p.m.*	*p.p.m.*	*pounds*
10	4	3.0	70	9.5	380	41.6	9.5	900
29	6	4.5	86	8.8	564	80.8	16.5	600
34	8	6.5	76	12.0	512	68.3	9.0	500
46	10	9.5	100	14.0	583	84.0	18.0	450
52	12	10.5	113	16.3	525	58.2	12.5	250
64	16	15.0	155	20.6	654	83.2	14.0	100
80	21	21.5	140	17.5	634	100.0	20.0	...
86	25	28.0	208	41.2	795	212.2	30.0	0
96	34	45.0	216	41.0	780	137.5	27.0	0
99	50	100.0+	416	115.6	2,154	660.0	152.0	0

close agreement of the *A. niger* method with the chemical method, although the total amount of phosphorus removed by the *A. niger* Niklas method is greater than that by any of the other methods. This high amount of phosphorus in the mold pad is due, no doubt, to the presence of 1 per cent of citric acid in the medium. The *A. niger* Simakova-Bovschik method and the *Cunninghamella* method show a good agreement with field results.

In order to determine further the reliability of the *Cunninghamella* method, soils of known phosphate needs from widely separated parts of the United States were obtained and tested by the *Cunninghamella* method and also by the Truog chemical method. The results of these tests, and also the response of these soils in the field, are presented in table 6. All in all, the results of the biological test agree fairly well with the field results. In cases where field

TABLE 6

Phosphate needs of 100 soils as revealed by Cunninghamella, *chemical, and field tests*

SOIL NO.	SOIL TYPE	REACTION OF SOIL	CUNNINGHAMELLA METHOD		TRUOG CHEMICAL METHOD	FIELD TEST RESPONSE TO PHOSPHATE
			Diameter of lateral growth	Amount of available phosphorus by curve interpolation	Amount of available phosphorus	
		pH	*mm.*	*p.p.m.*	*p.p.m.*	
1	Bladen fi. sa. lo.	4.0	0	0.0	Trace	Good
2	Gloucester fi. sa. lo.	5.0	0	0.0	16	Good
3	Norfolk fi. sa. lo.	5.5	3	2.0	Trace	Good
4	Wooster si. lo.	7.4	3	2.0	Trace	Good
5	Miami si. lo.	5.4	3	2.0	Trace	Good
6	Frederick si. lo.	5.2	4	3.0	Trace	Good
7	Norfolk sa. lo.	4.8	4	3.0	Trace	Good
8	Decatur cl. lo.	5.7	7	5.5	Trace	Good
9	Miami si. lo.	5.6	4	3.0	Trace	Good
10	Knox si. lo.	5.9	4	3.0	9.5	Good
11	Wooster si. lo.	6.3	4	3.0	4	Good
12	Wooster si. lo.	6.4	4	3.0	4	Good
13	Norfolk sa. lo.	5.8	4	3.0	18	Good
14	Merrimac fi. sa. lo.	5.2	4	3.0	24	Good
15	Napanee si. lo.	5.1	5	3.5	4	Good
16	Wooster si. lo.	6.6	5	3.5	8	Good
17	Huntington si. lo.	4.6	5	3.5	14	Good
18	Ontonagon cl. lo.	5.6	5	3.5	14	Good
19	Wisner si. lo.	8.3	5	3.5	76	Good
20	Dutchess si. lo.	5.5	5	3.5	8	Good
21	DeKalb si. lo.	6.0	6	4.5	4	Good
22	Saugatuck v. fi. sa.	4.6	6	4.5	Trace	Fair
23	Mannor lo.	5.5	6	4.5	Trace	Good
24	Wooster si. lo.	6.6	6	4.5	7	Good
25	Elkton si. lo.	4.0	6	4.5	8	Good
26	Hagerstown si. lo.	5.7	6	4.5	8	Good
27	Miami si. lo.	5.4	6	4.5	8	Good
28	Knox si. lo.	5.9	6	4.5	12	Good
29	Dodgeville si. lo.	6.6	6	4.5	16.5	Good
30	Wooster si. lo.	7.1	7	5.5	9	Good
31	Saugatuck fi. sa.	5.2	7	5.5	4	Fair
32	Porters lo.	6.0	7	5.5	Trace	Good
33	Canfield si. lo.	4.8	7	5.5	11	Good
34	Dodgeville si. lo.	6.7	8	6.5	9	Good
35	Wooster si. lo.	7.0	8	6.5	10	Good
36	Fox sa. lo.	5.6	8	6.5	23	Good
37	Upshur cl. lo.	4.0	9	7.3	17	Good
38	Dodgeville si. lo.	6.0	9	7.3	11.5	Fair
39	Knox si. lo.	5.9	9	7.3	12	Good

TABLE 6—*Continued*

SOIL NO.	SOIL TYPE	REACTION OF SOIL	CUNNINGHAMELLA METHOD		TRUOG CHEMICAL METHOD	FIELD TEST RESPONSE TO PHOSPHATE
			Diameter of lateral growth	Amount of available phosphorus by curve interpolation	Amount of available phosphorus	
		pH	*mm.*	*p.p.m.*	*p.p.m.*	
40	Orangeburg sa. lo.	5.6	9	7.3	6	Fair
41	Fox sa. lo.	4.6	10	8.5	18	Good
42	Brookston si. lo.	6.9	10	8.5	24	Fair
43	Merrimac fi. sa. lo.	4.8	10	8.5	40	Fair
44	Volusia si. lo.	4.8	11	9.5	16	Good
45	Maimi si. lo.	6.4	11	9.5	12	Fair
46	Miami si. lo.	6.3	11	9.5	18	Fair
47	Suffield cl. lo.	7.0	11	9.5	120	Fair
48	Caribou lo.	5.0	12	10.5	25	Fair
49	Hillsdale sa. lo.	6.0	13	11.5	20	Fair
50	Miami si. lo.	6.8	12	10.5	16	Fair
51	Miami si. lo.	5.8	12	10.5	12	Fair
52	Waukesha sa. lo.	5.5	12	10.5	12.5	Fair
53	Hawaii soil	5.2	12	10.5	20	None
54	Caribou lo.	4.9	13	11.5	34	Little
55	Westmoreland si. lo.	4.3	14	12.5	16	Fair
56	Dodgeville si. lo.	5.7	14	12.5	12	Fair
57	Sparta sa.	6.1	14	12.5	16	Fair
58	Wooster si. lo.	5.5	14	12.5	23	Good
59	Napanee si. lo.	6.3	14	12.5	40	Little
60	Muskingum fi. sa. lo.	4.3	15	14.0	Trace	Fair
61	Miami lo.	5.4	15	14.0	17	Fair
62	Hartselle fi. sa. lo.	5.8	15	14.0	24	Fair
63	Sassafrass lo.	5.4	16	15.0	16	Fair
64	Carrington si. lo.	5.4	16	15.0	14	Little
65	Marshall si. lo.	5.3	16	15.0	14	Fair
66	Marshall si. lo.	5.2	16	15.0	12	Fair
67	Muck	5.5	16	15.0	12	Fair
68	Cheshire fi. sa. lo.	5.4	16	15.0	47	Little
69	Marshall si. lo.	5.6	17	16.0	14	Little
70	Vergennes cl.	5.8	17	16.0	90	Little
71	Agawam fi. sa. lo.	5.3	18	17.5	33	Little
72	Carrington si. lo.	5.8	18	17.5	18	Little
73	Hagerstown si. lo.	5.0	18	17.5	22	Little
74	Ontario lo.	5.3	18	17.5	26	Little
75	Brookston lo.	6.3	18	17.5	30	Little
76	Wheeling fi. sa. lo.	6.0	19	19.0	20	Fair
77	Miami si. lo.	6.5	19	19.0	28	Little
78	Miami si. lo.	7.1	19	19.0	37	None
79	Miami si. lo.	5.8	20	20.0	27	Little
80	Carrington si. lo.	5.8	21	21.5	20	Little

TABLE 6—*Concluded*

SOIL NO.	SOIL TYPE	REACTION OF SOIL	CUNNINGHAMELLA METHOD		TRUOG CHEMICAL METHOD	FIELD TEST RESPONSE TO PHOSPHATE
			Diameter of lateral growth	Amount of available phosphorus by curve interpolation	Amount of available phosphorus	
		pH	*mm.*	*p.p.m.*	*p.p.m.*	
81	Carrington si. lo.	6.1	22	23.0	38	None
82	Dodgeville si. lo.	5.0	23	25.0	19	Little
83	Dodgeville si. lo.	5.0	24	26.0	15.2	Little
84	Thomas lo.	8.3	24	26.0	39	None
85	Cheshire fi. sa. lo.	5.5	24	26.0	132	None
86	Knox si. lo.	6.5	25	28.0	30	None
87	Wauseon lo. sa.	7.5	25	28.0	65	None
88	Miami si. lo.	6.4	26	29.5	74	None
89	Cheshire fi. sa. lo.	5.8	26	29.5	40	None
90	Superior cl.	5.0	28	33.0	26	
91	Miami si. lo.	5.0	28	33.0	28	None
92	Greenville sa. lo.	5.6	28	33.0	62	None
93	Merrimac fi. sa. lo.	6.4	30	37.0	64	None
94	Norfolk lo.	5.9	31	39.0	32	None
95	Hillsdale sa. lo.	6.5	33	43.0	53	None
96	Coloma sa. lo.	6.0	34	45.0	27	None
97	Hawaii soil	6.4	34	45.0	124	None
98	Carrington si. lo.	7.0	48	91.0	170	None
99	Willamette si. lo.	5.8	50	100.0+	152	None
100	Hawaii soil	5.8	50	100.0+	210	None

tests indicated a lack of phosphate, a poor development of *Cunninghamella* usually took place, and conversely, in cases where the field tests indicated an abundance of available phosphate, a luxuriant growth of the fungus, with a few exceptions, took place.

A special study was made of calcareous soils. The results are given in table 7. Without any preliminary treatment of soils of pH 7.5 or above, results with the *Cunninghamella* method are usually too low. The agreement of the test with field results was almost perfect for the soils responding to phosphate fertilizer, but only about 50 per cent for the calcareous soils not responding. When these soils are first neutralized with acid, as previously described, the agreement becomes quite satisfactory except with soils 114, 115, 125, 126, and 132. However, the subsoils of Nos. 114 and 115 as tested with the *Cunninghamella* method are well supplied with available phosphorus, and this probably explains why alfalfa grown on these soils does not respond to phosphorus fertilization. Soils 125, 126, and 132 come from areas of limited

moisture, and that may explain the lack of response to phosphate fertilization in the field.

TABLE 7

Phosphate needs of calcareous soils as revealed by Cunninghamella, *chemical, and field tests*

SOIL NUMBER	SOIL REACTION	$CaCO_3$ CONTENT OF SOIL	AMOUNT OF AVAILABLE PHOSPHORUS BY TRUOG CHEMICAL METHOD	CUNNINGHAMELLA METHOD			FIELD TEST RESPONSE TO PHOSPHATE
				Soil not treated	Soil neutralized with citric acid		
				Diameter of lateral growth	Diameter of lateral growth	Amount of available phosphorus by curve interpolation	
	pH	*per cent*	*p.p.m.*	*mm.*	*mm.*	*p.p.m.*	
101	8.4	2.15	12	3	6	4.5	Very good
102	8.1	25.35	6	5	9	7.0	Very good
103	8.4	1.78	70	5	9	7.0	Good
104	7.5	0.16	130	4	10	8.0	Good
105	8.5	6.52	8	3	8	6.0	Very good
106	7.5	0.49	80	4	8	6.0	Very good
107	8.6	8.34	8	3	10	8.0	Very good
108	8.5	1.82	14	6	8	6.0	Good
109	7.6	1.22	56	4	13	11.5	Good
110	8.1	2.31	64	6	12	10.5	Good
111	7.9	2.51	60	6	8	6.0	Good
112	8.1	4.46	30	5	10	8.0	Very good
113	8.0	2.03	26	8	27	31.5	None
114	8.3	3.89	18	8	20	20.0	None
115	7.5	0.28	53	8	18	17.5	None
116	7.8	0.65	92	7	29	35.0	None
117	8.2	4.54	106	5	30	37.0	None
118	8.2	7.00	290	6	52	100.0+	None
119	7.7	0.61	124	14	38	53.0	None
120	7.5	0.12	64	15	38	53.0	None
121	7.9	3.77	62	21	40	58.0	None
122	7.5	0.28	106	20	48	91.0	None
123	7.5	0.46	100	25	50	100.0+	None
124	7.4	0.08	68	37	40	58.0	None
125	8.0	2.34	26	..	12	10.5	None
126	8.1	9.80	5	..	11	9.5	None
127	7.5	0.41	112	..	50	100.0+	None
128	8.1	5.50	82	..	16	15.0	Little
129	8.9	7.90	45	..	7	5.5	
130	8.0	0.45	120	..	23	25.0	None
131	8.0	0.35	112	..	42	64.0	None
132	7.9	2.10	19	..	9	7.0	None

Results of the *Cunninghamella* test on 20 soils are compared with those of Mitscherlich's pot test on these soils in table 8. With the exception of soil 136, in which case the result with *Cunninghamella* is a little too high, the results compare favorably.

Practical application

The test using the fungus *Cunninghamella* for determining the phosphate needs of soils should find ready application, because of its simplicity, inexpensiveness, and reliability. The test may be made in any place where a room for incubation is at hand in which the temperature does not vary too greatly. Satisfactory results for practical purposes may be obtained at incubation temperatures ranging from 27° to 30°C. For experimental work, the temperature should be maintained at 28° to 29°C.

TABLE 8

Correlation of results of Cunninghamella *and Mitscherlich methods*

SOIL NUMBER	CUNNINGHAMELLA METHOD		MITSCHERLICH METHOD		
	Diameter of lateral growth	Amount of available phosphorus by curve interpolation	Amount of available phosphorus	Possible maximum crop yield	Need of phosphorus fertilization
	mm.	*p.p.m.*	*p.p.m.*	*per cent*	
134	6	4.5	5.4	29.2	Great
135	6	4.5	5.4	29.2	Great
136	26	29.5	32.4	87.4	Slight
137	18	17.5	40.7	92.7	Slight
138	19	19.0	43.0	93.7	Slight
139	21	22.0	47.2	95.2	Slight
140	27	31.5	53.6	96.8	No
141	24	26.0	53.6	96.8	No
142	32	41.0	57.8	97.5	No
143	28	33.0	60.4	97.8	No
144	40	58.0	62.1	98.1	No
145	40	58.0	73.0	99.0	No
146	38	53.0	75.0	99.2	No
147	43	67.0	75.0	99.2	No
148	25	28.0	79.5	99.4	No
149	24	26.0	82.3	99.6	No
150	22	23.0	94.3	99.7	No
151	50	100.0+	94.3	99.7	No
152	44	71.0	94.3	99.7	No
153	26	29.5	107.2	99.9	No

SUMMARY

A new simple biological soil plaque test, utilizing the fungus *Cunninghamella*, has been developed for measuring the phosphate needs of a soil. In making the test, the soil is moistened with a phosphorus-free nutrient solution and made into a plaque in a small Petri dish. One drop of the spore suspension is placed centrally on the surface. After incubation for about 48 hours, a colony develops, the diameter of which is closely proportional to the amount of available phosphorus present. In developing this test, a large number of

plaque tests were made with about 15 representative molds including several species of *Cunninghamella*. The influence of reaction, kind of nutrient solution, salt content, and supply of available phosphate was investigated. As a result of these studies, the fungus *Cunninghamella* sp. was chosen because of its sensitivity to a lack of, and marked progressive response to an increasing supply of, available phosphate. The test was compared with two *A. niger* methods, a chemical method, field tests, and Mitscherlich's method. The results obtained with many soils from widely separated areas show good agreement with field results. The test seems to work well with the calcareous soils that give great difficulty with some of the other methods.

REFERENCES

(1) BREAZEALE, J. F., AND BURGESS, P. S. 1926 The availability of phosphates in calcareous or alkaline soils. *Ariz. Agr. Exp. Sta. Tech. Bul.* 10: 209–237.

(2) BREAZEALE, J. F., AND MCGEORGE, W. T. 1932 Nutritional disorders in alkaline soils as caused by deficiency of carbon dioxide. *Ariz. Agr. Exp. Sta. Tech. Bul. 41*: 113–153.

(3) LESCH, W. 1933 Beitrag zur Kenntnis des Einflusses des Kalkzustandes eines Bodens auf die Aufnahmefähigkeit der Pflanzen für Phosphorsäure und Kali. *Ztschr. Pflanzenernähr., Düngung, u. Bodenk.* (A) 32: 20–32.

(4) MEHLICH, A., TRUOG, E., AND FRED, E. B. 1933 The *Aspergillus niger* method of measuring available potassium in soil. *Soil Sci.* 35: 259–279.

(5) MITSCHERLICH, E. A. 1930 Die Bestimmung des Düngerbedürfnisses des Bodens. P. Parey, Berlin.

(6) NIKLAS, H., POSCHENRIEDER, H., AND TRISCHLER, J. 1930 Die Kultur des Schimmelpilzes *Aspergillus niger* zur biochemischen Bestimmung der Kali- und Phosphorsäuredüngebedürftigkeit der Böden. *Ernähr. Pflanze* 26: 97–103.

(7) NIKLAS, H., POSCHENRIEDER, H., AND TRISCHLER, J. 1931 Eine neue mikrobiologische Methode zur Feststellung der Düngebedürfigkeit der Böden. *Arch. Pflanzenbau* 5: 451–485.

(8) NIKLAS, H., VILSMEIER, G., AND KOHL, F. 1933 Die Bestimmung der Phosphorsäuredüngebedürftigkeit der Böden mittels *Aspergillus niger*. *Ztschr. Pflanzenernähr. Düngung u. Bodenk.* (A) 32: 50–70.

(9) SIMAKOVA, T., AND BOVSCHIK, G. 1932 Ueber die mikrobiologische Methode zur Bestimmung des Phosphorbedürfnisses des Bodens mittels *Aspergillus niger*. *Ztschr. Pflanzenernähr. Düngung, u. Bodenk.* (A) 24: 341–353.

(10) STEWART, R. 1932 The Mitscherlich, Wiessmann and Neubauer methods of determining the nutrient content of soils. *Imp. Bur. Soil Sci. Tech. Comm.* (London) 25: 46 pp.

(11) TRUOG, E. 1930 The determination of the readily available phosphorus of soils. *Jour. Amer. Soc. Agron.* 22: 874–882.

PLATE 1

PLATE 1

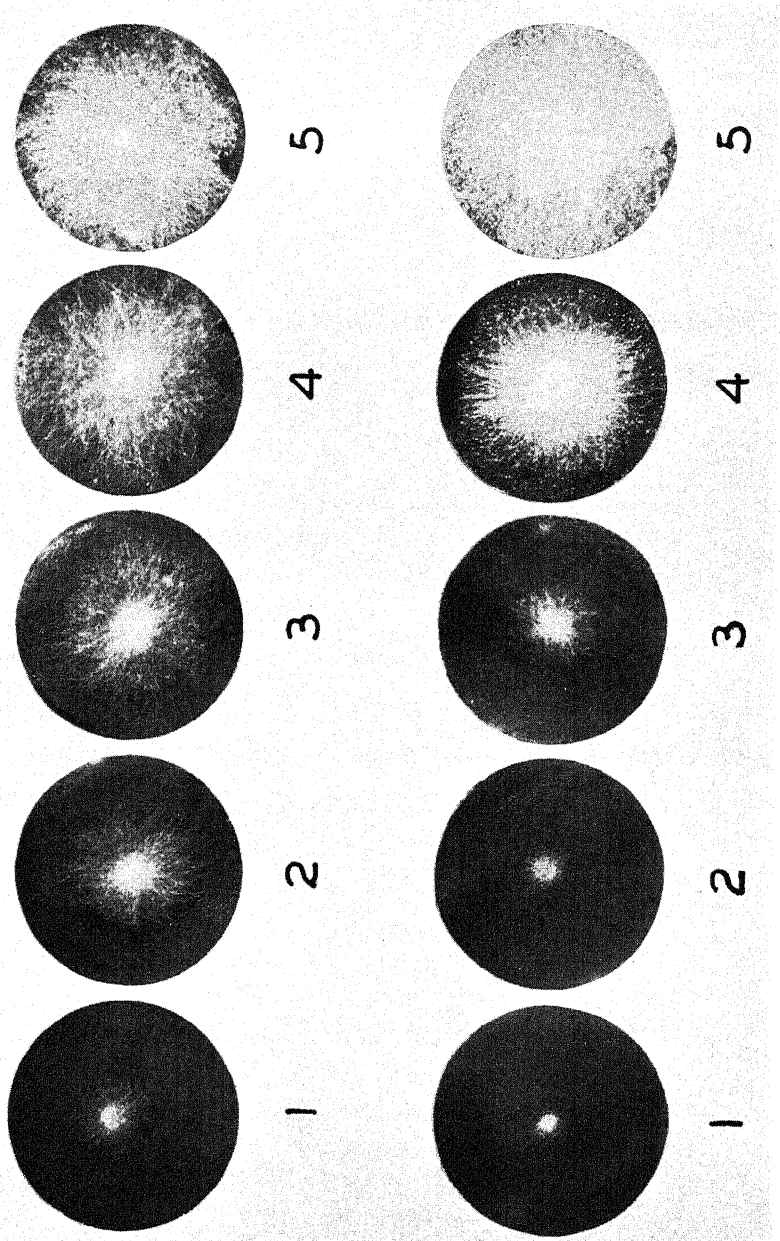
GROWTH OF CUNNINGHAMELLA ON SOILS WITH DIFFERENT AMOUNTS OF AVAILABLE PHOSPHORUS

Upper row: A soil containing 12 p.p.m. available phosphorus and treated with the following increasing amounts of soluble phosphorus:

No. 1— 0 p.p.m.
No. 2—20 p.p.m.
No. 3—40 p.p.m.
No. 4—60 p.p.m.
No. 5—80 p.p.m.

Lower row: Soils, untreated, containing the following amounts of available phosphorus, as revealed by chemical method:

No. 1 contains	4 p.p.m.	Responds markedly to phosphate in the field.
No. 2 contains	12 p.p.m.	Responds markedly to phosphate in the field.
No. 3 contains	17 p.p.m.	Responds moderately to phosphate in the field.
No. 4 contains	64 p.p.m.	No response to phosphate in the field.
No. 5 contains	152 p.p.m.	No response to phosphate in the field.


5
4
3
2
1
5
4
3
2
1

EFFECT OF THE DEGREE OF BASE SATURATION OF A SOIL ON ITS CAPACITY TO FIX PHOSPHORUS IN DIFFICULTLY AVAILABLE FORM[1]

A. FLOYD HECK[2]

Wisconsin Agricultural Experiment Station

Received for publication January 31, 1934

Soils well supplied with lime and not more than slightly acid have been found less frequently deficient in readily available phosphorus than have more acid soils. The effect of the calcium on the mass action equilibrium with phosphorus and also the effect of the higher pH value on the relative solubilities of phosphates (2) are perhaps, largely responsible for this tendency. In the same way, the amount of active or replaceable calcium affects the equilibrium which governs the fixation of applied phosphorus in a difficultly available form. Soils from which the exchangeable bases have been removed fix more phosphorus in difficultly available form, and the increase is somewhat in proportion to the bases removed. The effect of the degree of base saturation in two widely different soils has been studied in its relation to the fixation of phosphorus and is herein reported. In this paper, "phosphorus fixation" will be understood to mean the change from the quickly or readily available form to the slowly or difficultly available forms or to forms very slightly soluble in sulfuric acid of pH 3.

EXPERIMENTAL

The soils used for this study were Miami silt loam, a glaciated timber soil from Wisconsin, and a Hawaiian laterite from the Waipio Substation, Experiment Station of the Hawaiian Sugar Planters' Association. From its colloidal content, this laterite might be characterized as a clay or clay loam, but because of its lateritic characters its physical properties in the field would probably place it in the loam class.

Portions of each soil were entirely unsaturated and other portions saturated to various degrees with calcium. Unsaturation was accomplished by leaching out all replaceable bases with 0.1*N* acetic acid. The saturated condition was obtained by leaching the soil with 0.5*N* neutral calcium acetate solution; and the partially saturated condition, by leaching calcium saturated 40-gm. samples with carbonated water in amounts varying from 50 to 4,000 cc. The

[1] Contribution from the department of soils, University of Wisconsin, Madison, Wisconsin. Published with the permission of the director of the Wisconsin Agricultural Experiment Station.

[2] The writer is appreciative of the kindly coöperation of Prof. E. Truog.

soils were then dried and pulverized, and the capacity of each to fix applied phosphorus was determined.

In view of the fact that a soil is theoretically saturated only when a pH value of 14 is reached, it will be necessary for the discussion in this paper to define "saturation" as that state of base saturation obtained by leaching the soil with 0.5*N* neutral calcium acetate solution. This state of base saturation will be considered as 100 per cent saturation, and all partial saturations will be based thereon.

The pH values were determined by means of the hydrogen electrode and checked by Truog's colorimetric method (Truog soil reaction tester). The

TABLE 1

The relation of base saturation and pH value of Miami silt loam and Waipio soil to their capacities to fix phosphorus in difficultly available form

SOIL TREATMENT	MIAMI SILT LOAM			WAIPIO SOIL		
	Calcium in exchange	pH value	Capacity to fix phosphorus	Calcium in exchange	pH value	Capacity to fix phosphorus
	m.e.		*per cent*	*m.e.*		*per cent*
Original soil, untreated	8.20*	5.94	25.0	15.40†	6.74	67.0
Soil saturated with calcium	11.37	7.20	22.5	19.50	8.03	62.5
Ca-saturated soil leached 50 cc. CO_2-water	9.91	6.02	23.7	17.15	7.55	62.0
" " " " 100 cc. " "	9.22	5.50	27.5	14.25	6.84	64.7
" " " " 200 cc. " "	8.37	5.10	32.5	11.85	6.22	70.5
" " " " 500 cc. " "	7.10	4.80	36.7	9.50	5.55	76.2
" " " " 1,000 cc. " "	5.69	4.45	41.0	7.05	5.09	80.0
" " " " 2,000 cc. " "	4.69	4.20	43.0	4.10	4.67	80.0
" " " " 4,000 cc. " "	3.90	3.80	45.0	1.80	4.24	81.2
Soil saturated with hydrogen	0.00	3.55	45.0	0.00	3.87	82.7

* Total exchangeable bases including 6.45 m.e. of calcium.

† Total exchangeable bases including 8.25 m.e. of calcium and 6.3 m.e. of magnesium.

capacity of the soil to fix phosphorus in difficultly available form was determined by a method proposed by the writer (3) after an application of 400 p.p.m. of phosphorus in solution.

The data for both soils are given in table 1, and include the exchangeable calcium, the pH values, and the capacity of each soil to fix phosphorus in difficultly available form, both before and after the treatment to vary the content of exchangeable calcium.

Relation of hydrogen-ion concentration to the fixation of phosphorus. If the pH values of either of these soils are converted into hydrogen-ion concentrations and the phosphorus fixation percentages are plotted against these values, curves are obtained like that for the Miami silt loam shown in figure 1. This

figure shows that the rate of increase in the capacity of a soil to fix phosphorus in difficultly available form is greatest for any given increment of hydrogen-ion concentration in the range from 0.01×10^{-5} to 0.50×10^{-5}. Above a hydrogen-ion concentration of 1×10^{-5} (pH 5), the increment of fixation drops off very rapidly, and above 6×10^{-5} there is very little further increase in fixation. Figure 1 indicates that although the total may be greater, the

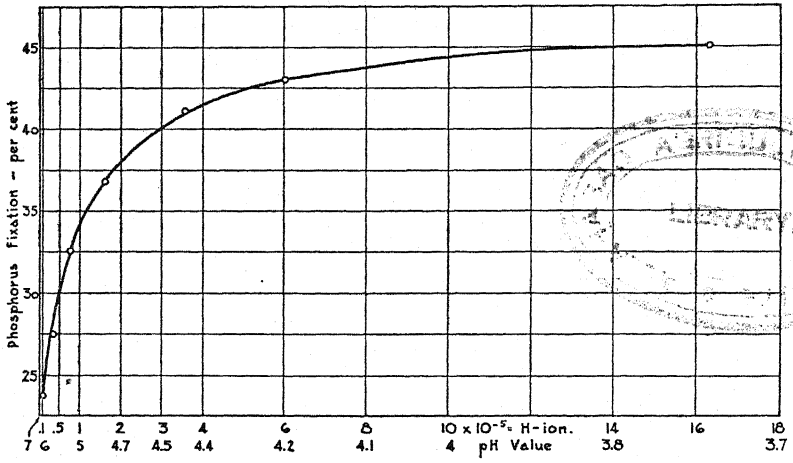


FIG. 1. THE RELATION OF HYDROGEN-ION CONCENTRATION TO PHOSPHORUS FIXATION IN MIAMI SILT LOAM

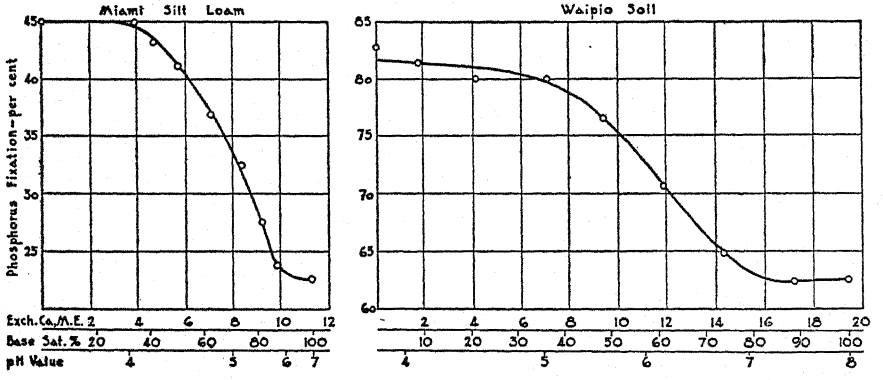


FIG. 2. THE RELATION OF EXCHANGEABLE CALCIUM TO PHOSPHORUS FIXATION

rate of reduction of the capacity of a soil to fix phosphorus in difficultly available form is much more rapid after the pH value of the soil is raised above 5. This same relation also holds true for the Waipio soil.

Relation of exchangeable calcium to phosphorus fixation. If the fixation capacities expressed in percentages of the applied phosphorus fixed in difficultly available form for these two soils are plotted against the milliequivalents of

exchangeable calcium present, there are two breaks in each curve. One break comes near the upper limit of base saturation, above which there is little decrease in fixation, and the other comes toward the lower end of the saturation scale, below which there is little increase in the fixation of phosphorus. These relations for Miami silt loam and the Waipio soil are shown in figure 2. For both soils, the break in the fixation curve at the lower saturations comes at about 30 to 35 per cent base saturation. This is about pH 4 for the Miami silt loam and pH 5 for the Waipio soil. The break in the fixation curve at the higher base saturations for the Miami silt loam comes at about 92 per cent saturation, while for the Waipio soil this value drops to about 82 per cent. For the former soil, the pH value at this break in the

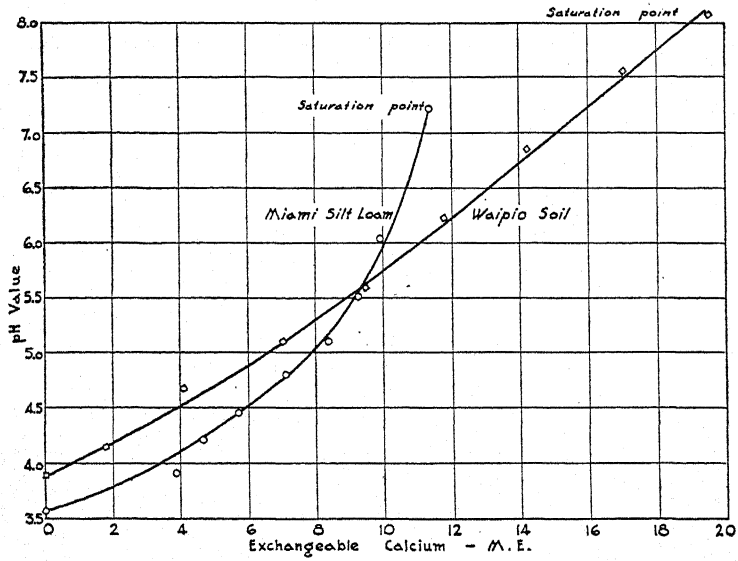


FIG. 3. RELATION OF EXCHANGEABLE BASE (CALCIUM) TO THE pH VALUES OF MIAMI SILT LOAM AND WAIPIO SOIL

curve is about 6.3, while for the latter it is 7.0 to 7.3. It appears that there is a closer relationship of the upper and the lower breaks in the fixation curves to the percentage base saturations than to the pH values.

Minimum fixation in a soil may be very high or very low, depending upon the nature of the soil, but it is not attained at less than 80 to 90 per cent base saturation. In a soil of normal organic content, 90 per cent base saturation will produce a pH value of about 6.3 to 6.5. This correlates with the work of Gaarder (2) in which he has shown that the minimum solubility of phosphorus from calcium phosphate is obtained at pH 6.5 to 7.0. According to his work, at this pH value the phosphorus from calcium phosphate has a solubility of only one-third to one-fourth that of aluminum or iron phosphate.

The shapes of the fixation curves for these two soils differ somewhat, but

the outstanding difference is the pH value at the breaking point of minimum fixation. This difference in the pH value at the breaking point of minimum fixation for the two curves is probably due, in a small part, to the difference in the exchange capacities but, for the most part, to the nature of the exchange materials of these two soils. In figure 3, the pH values for each soil are plotted against the corresponding values for exchangeable calcium, and the resulting curves indicate that the two soils are vastly different in this relationship. The curve for the Waipio soil is nearly a straight line, which indicates the presence, perhaps to a large extent, of only a single exchange complex. In case of the Miami silt loam, there appears to be more than one complex, suggesting the presence of both the organic and the inorganic forms of this substance. This is in accord with the work of Mitchell (6), who reported a high proportion of the organic exchange material in both Carrington and

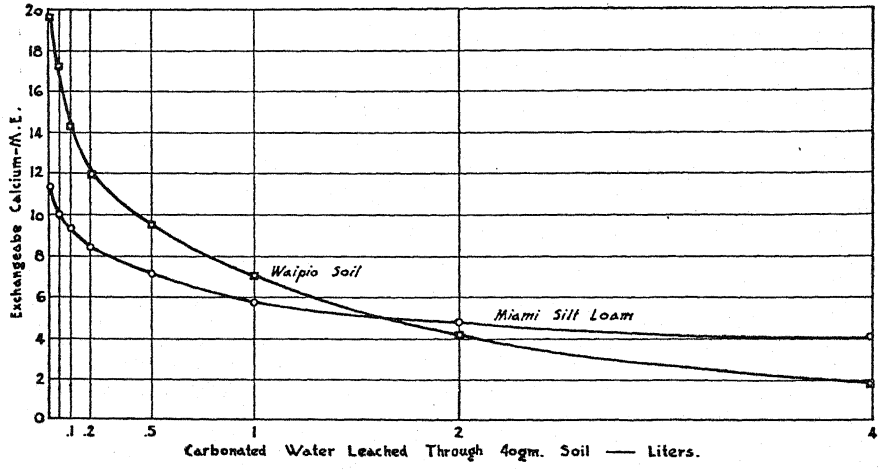


FIG. 4. EXCHANGEABLE CALCIUM RETAINED BY MIAMI SILT LOAM AND WAIPIO SOIL WHEN THE CALCIUM SATURATED SOILS ARE LEACHED WITH CARBONATED WATER

Dodgeville silt loams. Since the inorganic exchange complex is thought to be monobasic and the organic form either dibasic or tetrabasic (4), the chances are that the avidity of these two acids will not be the same and that the organic form will tend to have the greater avidity, which would result in a lower pH value for the same percentage base saturation. The leaching curves in figure 4 indicate that Miami silt loam loses its exchange calcium less readily when leached with carbonated water. This fact, together with the fact that 92 per cent base saturation for Miami silt loam gives a pH value of approximately 6.5 whereas the same base saturation for the Waipio soil gives a pH value of about 7.7, indicates a greater avidity for the acid organic exchange material of the Miami silt loam. This may partially explain why the pH values at minimum fixation for these two soils differ so widely and seem inconsistent with the degree of base saturation at this point.

Although the capacity of the Miami silt loam to fix phosphorus may be relatively low and that for the Waipio soil relatively high, the spread between the maximum and minimum fixation in the two soils is about the same—22.5 per cent for the former and 20 per cent for the latter. The spread between the maximum and minimum fixation percentages for any soil due to variation in base saturation, may perhaps run as high as 30 per cent but seldom runs more than this. Ford (1) has shown that by using an excess of lime on some soils the fixation in difficultly available form may be reduced to a very small amount, but this excess of lime is so large that its use is not practical in the field either from the standpoint of cost or from the difficulty arising from overliming (5).

Other factors related to base saturation and fixation. The amount of exchange material present in a soil, the extent to which the soil is saturated with bases, and also the amount and kind of the base carried by the phosphate itself are other factors which affect the extent to which phosphorus is fixed in difficultly available form. Samples of the Waipio soil were treated either with monocalcium or tricalcium phosphate in various combinations with calcium and the hydrogen saturated inorganic exchange complex. These samples were made up to optimum moisture and allowed to stand at room temperature, and the phosphate fixation being determined at intervals of 2, 10, 20, 40, and 80 days. The treatments were as follows:

1. Monocalcium phosphate.
2. Monocalcium phosphate + 4 m.e. calcium.
3. Monocalcium phosphate + 4 m.e. acid exchange material (inorganic).
4. Monocalcium phosphate + 4 m.e. acid exchange material and 4 m.e. calcium.
5. Monocalcium phosphate + 4 m.e. acid exchange material and 8 m.e. calcium.
6. Tricalcium phosphate.
7. Tricalcium phosphate + 4 m.e. calcium.

Since this soil lacked just 4 m.e. of being saturated with base, the addition of this amount just saturated the exchange to pH 7. This was added as calcium hydroxide in solution. Figure 5 shows how each of these treatments affects the recovery of applied phosphorus in readily available form. It is understood that the phosphorus not recovered in readily available form was fixed in difficultly available form.

When monocalcium phosphate is applied to this soil, the amount that may be recovered in readily available form drops off very rapidly at first and then more slowly later until at the end of 80 days only about 25 per cent in still readily available (curve 1). If the 4 m.e. of replaceable hydrogen in this soil is replaced with calcium (curve 2), the recovery curve runs a few per cent higher and practically parallel with curve 1. Now if 4 m.e. of hydrogen saturated inorganic exchange material is added (curve 3), the curve drops below that for the soil treated with the monocalcium phosphate alone but is still parallel with it. With the addition of 4 m.e. of calcium (curve 4) to a

soil treated as is soil 3, the recovery is greater at first but finally drops and coincides with curve 3. This treatment supplied only half enough calcium to displace the replaceable hydrogen, but when 8 m.e. of calcium is added (curve 5), or enough to completely saturate the exchange with calcium, the recovery is raised to about 42 per cent at 80 days. This indicates that as the amount of exchange material is increased, the exchangeable bases must also be increased in order to maintain or increase the recovery of applied soluble phosphorus in readily available form. However, other factors being equal, an increase in the exchange capacity of a soil accompanied by an 80 to 90 per cent base saturation tends to raise the recovery and lower the fixation of applied soluble phosphate.

Although the fixation curves for the mono- and tricalcium phosphate are practically parallel after the first day, the initial fixation is 20 per cent less for

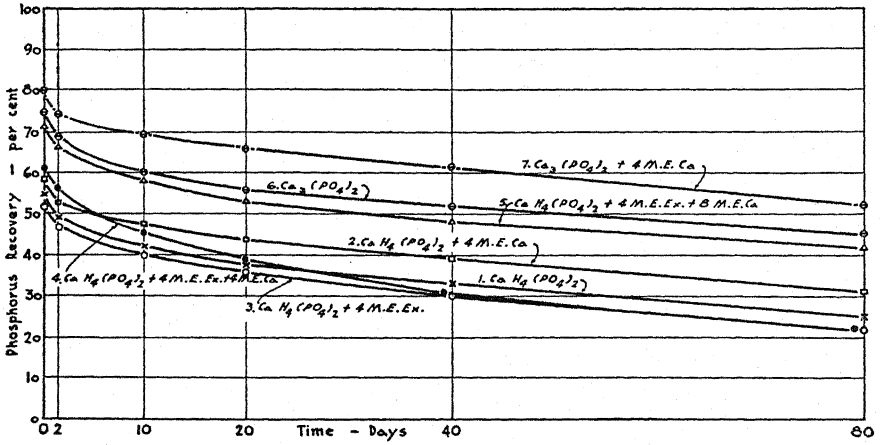


FIG. 5. THE EFFECT OF EXCHANGEABLE CALCIUM AND EXCHANGE MATERIAL ON THE RECOVERY IN READILY AVAILABLE FORM OF PHOSPHORUS APPLIED TO WAIPIO SOIL

the tricalcium form. When the exchange is saturated with calcium, the increase from this saturation in the recovery of applied soluble phosphate is even greater from the tricalcium than from the monocalcium form. Both the solubility of the phosphate and the amount of calcium present seem to affect the fixation equilibrium, and the more calcium present the greater is the tendency for the phosphorus to be held in the calcium form, which results in a lower initial fixation.

DISCUSSION

The maximum change in extent of phosphorus fixation that may be effected by a change in the degree of base saturation is seldom more than 30 per cent and usually not more than 20 per cent of the applied phosphorus. High and low fixing soils are affected to about the same extent. In a soil fixing 35 per

cent, the fixation would be reduced to 10 or 15 per cent by sufficient base saturation, whereas a soil having a 75 per cent maximum fixation would still fix over 50 per cent of the applied phosphorus in difficultly available form.

In high fixing soils that are rather acid, a small field application of lime may even double the availability of the applied phosphorus. If such a soil, fixing 90 per cent of the applied phosphorus, is limed sufficiently to raise the pH value to 5.0 to 5.4, the fixation may be reduced to 80 per cent, which would double the amount of readily available phosphorus from applied superphosphate. With a crop like potatoes, where it is not advisable to raise the pH value above 5.0 to 5.2, there are indications that just such an effect is produced in the field on this type of soil.

SUMMARY

A study was made of the relation of the base saturation of Miami silt loam and of Waipio soil (laterite) to the capacities of these soils to fix applied phosphorus in difficultly available form. The results obtained with these soils seem to justify the following conclusions:

A low degree of base saturation tends to give a soil a greater capacity for fixing phosphorus in difficultly available form than if the soil is more fully saturated with bases.

Minimum phosphorus fixation for a soil is attained at from 80 to 90 per cent base saturation. For soils having a fair proportion of organic exchange material, this point comes toward the higher value. At the same time, these soils will tend to have a lower pH value at the point of minimum fixation than soils in which the exchange complex is largely inorganic; the breaking point of the former being near 6.3, while for the latter it is from 7.0 to 7.5.

The variation in phosphorus fixation that may be brought about by a change in the base saturation of a soil does not usually exceed 20 to 30 per cent of the phosphorus applied. There appears to be little difference in this spread for high or low fixing soils.

Increased exchange capacity of a soil tends to decrease phosphorus fixation, provided the proper degree of base saturation is maintained. If sufficient base saturation is not maintained, increased exchange capacity tends to increase the capacity of a soil to fix phosphorus in difficultly available form.

REFERENCES

(1) FORD, M. C. 1933 The nature of phosphate fixation in soils. *Jour. Amer. Soc. Agron.* 25: 134–144.

(2) GAARDER, T. 1930 Die Bindung der Phosphorsäure im Erdboden. Vestlandets Forstl. Forsøkssta. Meddel. 14.

(3) HECK, A. FLOYD 1934 A method for determining the capacity of a soil to fix phosphorus in difficultly available form. *Soil Sci.* 37: 477–482.

(4) MCGEORGE, W. T. 1931 Organic compounds associated with base exchange reactions in soils. Ariz. Agr. Exp. Sta. Tech. Bul. 31.

(5) MIDGLEY, A. R. 1932 Overliming acid soils. *Jour. Amer. Soc. Agron.* 24: 822–836.

(6) MITCHELL, J. 1932 The origin, nature, and importance of soil organic constituents having base exchange properties. *Jour. Amer. Soc. Agron.* 24: 256–275.

THE SOLUBILITY OF PHOSPHORUS IN SOILS FROM SOME ILLINOIS EXPERIMENT FIELDS

H. J. SNIDER

Illinois Agricultural Experiment Station[1]

Received for publication January 15, 1934

The fact that certain soils respond to phosphate treatment and others do not has long been observed in field tests. This difference has been attributed to various causes. It has often been assumed that soils containing an abundant supply of total phosphorus would show little if any response to phosphorus fertilization, whereas, on the other hand, soils with a low content of total phosphorus would respond sharply to such treatment. Many exceptions, however, are found to this expected behavior, and it is quite apparent that response to phosphorus treatment is not necessarily dependent upon the total phosphorus content of soils.

It has been pointed out that soils vary in their power to fix phosphorus, and it is known that fixation by the soil renders the phosphorus less available to plants. Some years ago Stoddard (11) called attention to the possibilities of iron and aluminum compounds fixing phosphates in acid soils. Fraps (9, 10) in reporting his experiments pointed out that as larger amounts of iron and aluminum oxides were found in soils the amount of phosphorus fixed by the soils increased. Comber (5) comments on the fixing of phosphates by iron, aluminum, and calcium. Doughty (6), working with peat soils, states that iron, aluminum, and calcium will account for the fixation of phosphates under field conditions. Teakle (12) shows the possibility that iron, aluminum, manganese, and calcium fix phosphorus. Truog (16) states that yellow-colored soils fix phosphorus more readily than do red-colored soils, because of a difference in the form of iron compounds in these soils. He states further that phosphorus becomes less available, as a result of the interaction of soil phosphates with hydrated iron oxides, forming basic iron phosphates.

PLAN OF THE PRESENT STUDY

An opportunity to study this problem further is afforded by the several soil experiment fields conducted by the University of Illinois in various parts of the state, and the following observations are presented as the record of such a study on a number of these fields. The fields studied represent a number

[1] Contribution from the department of agronomy. Publication authorized by the director January 10, 1934.

of soil types, and they had been under systems of soil treatment for 15 to 22 years. The method of study involved the following procedure:

A determination of the relative solubility of the native phosphorus in soils from treated and untreated field plots.

A determination of the relative ability of the soils from various fields to fix phosphorus.

A study of the crop response of these soils to phosphorus treatment.

DESCRIPTION OF EXPERIMENT FIELDS

On these fields limestone was applied to certain plots at the rate of 1,000 pounds an acre annually, and was continued at this rate until the total reached 8 to 10 tons an acre. During the last 9 years no limestone was added.

A crop residue treatment consisting of cornstalks and a growth of sweet clover turned under once in the rotation as a green manure has been employed. The sweet clover has made a considerable growth only on the limed plots, except on the Hartsburg field where it produces heavy crops on unlimed soil.

The percentage increase in crop yield due to rock phosphate (table 1) represents the percentage value of the crop increase where rock phosphate was used in addition to crop residues and limestone. The rock phosphate was applied at the annual rate of 500 pounds an acre until a total of 4 tons had been added to the soil. A detailed description of the fields and analyses of the crop yields have been given by Bauer (1, 2, 3, 4).

ANALYTICAL METHODS

The phosphorus solubility determinations were made according to the Truog (14) method using 2 gm. soil to 400 cc. of 0.002 *N* buffered H_2SO_4 with the time of extraction extended to 4 and 5 hours.

The relative fixation of phosphorus was determined by adding in solution 50 ppm. of phosphorus as $CaH_4(PO_4)_2$ to 2 gm. of soil. This was allowed to stand in contact with the soil in an open flask at room temperature for 44 to 48 hours, after which it was extracted by the method already indicated except that the time was shortened to one-half hour. A method similar to this was reported by Doughty (6).

SOLUBILITY AND FIXATION RESULTS

The solubility results in figure 1 and table 1 show a wide variation in the amounts of soluble phosphorus obtained from these soils. In some of the soils the solubility greatly increased as the extraction was continued up to 5 hours, as illustrated in figure 1, whereas in others little or no change in solubility occurred after the first half hour of extraction. This difference in solubility along with the differences in value of crop response to phosphorus treatment serves as a basis for placing the fields in rather well-defined groups with respect to phosphorus availability.

The Lebanon and Hartsburg fields are placed in Group I. These soils show relatively high solubility values, increasing greatly with the length of

TABLE 1

Effect of treatment on the solubility and fixation of phosphorus in soils

GROUP	FIELD AND SOIL TYPE	PLOT TREATMENT	SOLUBLE PHOSPHORUS EXTRACTED IN		PHOSPHORUS FIXED	INCREASE IN YIELD DUE TO ROCK PHOSPHATE
			½ hr.	4 hrs.		
			p.p.m.	*p.p.m.*	*per cent*	*per cent*
I	Hartsburg					
	Grundy clay loam	None	40	120	34	5.0
		R*	44	120	34	
		RL†	55	130	22	
	Lebanon					
	Grundy silt loam	None	13	27	30	6.0
		R	13	30	30	
		RL	25	49	21	
II	Toledo					
	Cisne silt loam	None	8	9	48	−10.9
		R	8	9	48	
		RL	12	17	36	
	Sparta					
	Wynoose silt loam	None	6	7	60	−5.5
		R	6	7	60	
		RL	10	15	40	
	Dixon					
	Muscatine silt loam	None	8	9	48	2.3
		R	8	9	48	
		RL	13	19	38	
	Clayton					
	Grundy silt loam	None	6	7	50	2.9
		R	6	7	50	
		RL	11	17	36	
III	Kewanee					
	Muscatine silt loam	None	6	8	54	12.2
		R	6	8	54	
		RL	10	12	42	
	West Salem					
	Bluford silt loam	None	6	6	56	34.9
		R	6	6	56	
		RL	9	10	44	
	Joliet					
	Clarion silt loam	None	9	9	54	41.1
		R	9	9	54	
		RL	9	12	42	
	Elizabethtown					
	Yellow silt loam	None	6	6	62	60.2
		R	6	6	62	
		RL	6	7	54	

* R—crop residues.

† RL—crop residues and limestone.

time extracted. They have, on the other hand, relatively low fixing values, and they show comparatively low percentage increases in crop yields due to added phosphorus. The limestone treatment on these soils increased the solubility of the native phosphorus and also lowered the percentage phosphorus fixed.

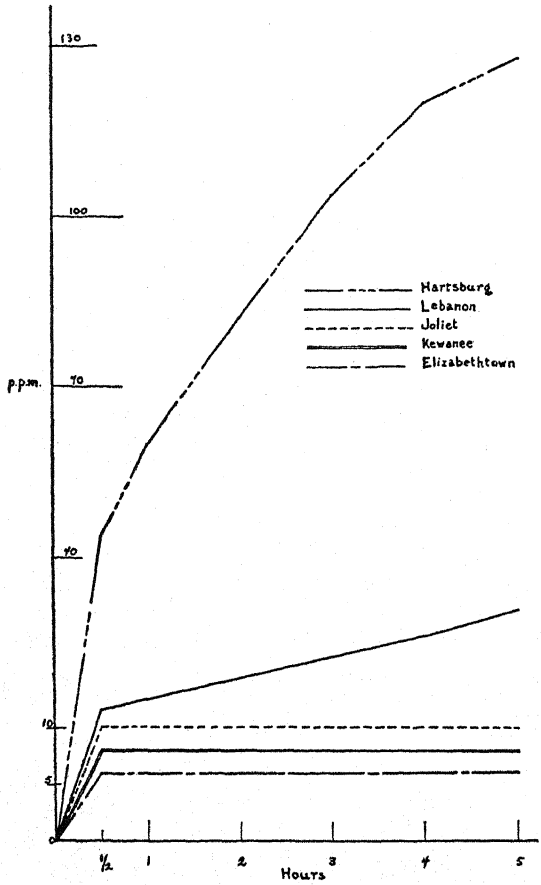


FIG. 1. SOLUBILITY CURVES SHOWING THE EFFECT OF TIME UPON THE AMOUNT OF PHOSPHORUS EXTRACTED FROM DIFFERENT SOILS

From the results given in table 1 it would seem that the soils in Group I are well supplied with available phosphorus which is usable by the growing crop. The addition of rock phosphate to these soils gives only 5 or 6 per cent increases in crop yields.

The Toledo, Sparta, Dixon, and Clayton fields are placed in Group II. These soils show relatively low solubility values on the untreated plots with little or no increase in solubility as the time of extraction was increased up to

4 hours. The soils on these fields have relatively high values for phosphorus fixed and extremely low, or even negative, values for percentage increase in crop yield due to phosphate treatment. The addition of limestone to soils of this group has increased the solubility of the native phosphorus. This greater solubility is more evident when the time of extraction was lengthened to 4 hours.

This increased solubility of the native phosphorus due to the crop residue-limestone treatment apparently made available to the crops sufficient phosphorus to offset the influence of the phosphorus added as rock phosphate.

These results seem to bear out the statement of Ellett (8) that lime acts upon iron compounds in the soil with the effect of making some of the phosphorus available. Truog (13, 15) states that the use of an abundance of lime prevents the interaction of iron oxides with soil phosphates and keeps phosphorus in the form of easily available calcium phosphate.

The Kewanee, West Salem, Joliet, and Elizabethtown fields are placed in Group III. The soils of this group had relatively low solubility values on the untreated plots, as indicated in table 1. The treated soils differed from those of Group II as there was not a large increase in the solubility of the native phosphorus through the influence of the crop residue-limestone treatment.

Apparently there was not sufficient increase in the availability of the native phosphorus caused by the crop residue-lime treatment on these soils to offset the increase in crop yields made by the applied phosphate. The percentages for crop increases in this group ranged from 12.2 up to 60.2 for the phosphorus treatment. This group produced by far the largest increase in crop yield due to applied phosphorus. The percentage phosphorus fixed by the soils of this group was relatively high, and the percentage phosphorus fixed by the soils from the crop residue-lime treatment was higher than that of a similar treatment in the other two groups.

SUMMARY

A study of the availability of phosphorus on a number of the Illinois soil experiment fields has furnished the following information:

The soils studied vary both in solubility of phosphorus and in their power to fix phosphorus.

The solubility and fixation were influenced by the crop residues-limestone treatment.

In general the soils having the lowest relative solubility and the highest relative fixing power gave the greatest response to rock phosphate as measured by increase in crop yields.

The fields studied may be divided into three groups as follows:

a. Those fields representing soils containing a sufficient supply of available native phosphorus so that additional phosphorus applied as a fertilizer is of little value in crop production.

b. Those fields representing soils having a low value for soluble phosphorus on the untreated check plots but with the availability of the native phosphates increased by the crop residue-lime treatment, thus rendering added phosphorus in the form of fertilizer of little value.

c. Those fields representing soils having low availability of phosphorus on the untreated checks but on which the crop residue-lime treatment did not affect the availability of the native phosphorus sufficiently to offset the value of added phosphorus, thus causing the soils of this group to show significant response to phosphorus treatment.

REFERENCES

(1) BAUER, F. C. 1927 Crop yields from Illinois experiment fields. Ill. Agr. Exp. Sta. Bul. 305.

(2) BAUER, F. C. 1930 Crop yields from Illinois experiment fields. Ill. Agr. Exp. Sta. Bul. 370.

(3) BAUER, F. C. 1931 Crop yields from Illinois experiment fields. Ill. Agr. Exp. Sta. Bul. 382.

(4) BAUER, F. C., SMITH, R. S., AND SMITH, L. H. 1926 The Illinois experiment fields. Ill. Agr. Exp. Sta. Bul. 273.

(5) COMBER, N. M. 1924 The rôle of electronegative ions in the reactions between soils and electrolytes. *Trans. Faraday Soc.* 1924: 567–572.

(6) DOUGHTY, J. L. 1930 The fixation of phosphorus by peat soils. *Soil Sci.* 29: 23–35.

(7) DOUGHTY, J. L. 1931 Phosphorus studies of Alberta soils. *Sci. Agr.* 12: 43–51.

(8) ELLETT, W. B. 1910 Lime for Virginia farms. Va. Agr. Exp. Sta. Bul. 187.

(9) FRAPS, G. S. 1909 Active phosphoric acid and its relation to the needs of the soil for phosphoric acid in pot experiments. Tex. Agr. Exp. Sta. Bul. 126.

(10) FRAPS, G. S. 1922 The fixation of phosphoric acid by soils. Tex. Agr. Exp. Sta. Bul. 304.

(11) STODDARD, C. W. 1909 Phosphate availability in its relation to soil acidity. *Wis. Agr. Exp. Sta. Res. Bul.* 2: 50–60.

(12) TEAKLE, L. J. H. 1928 Phosphate in the soil solution as affected by reaction and cation concentration. *Soil Sci.* 25: 143–161.

(13) TRUOG, E. 1916 The utilization of phosphates by agricultural crops including a new theory regarding the feeding power by plants. Wis. Agr. Exp. Sta. Res. Bul. 41.

(14) TRUOG, E. 1930 Determination of the readily available phosphorus of soils. *Jour. Amer. Soc. Agron.* 22: 874–882.

(15) TRUOG, E. 1930 The pH requirement of cultivated plants in natural and artificial cultures. *Amer. Nat.* 64: 300–313.

(16) TRUOG, E., AND FORD, M. C. 1930 New science for an old art. Wis. Agr. Exp. Sta. Bul. 410: 6–8.

A METHOD FOR DETERMINING THE DEGREE OF DECOMPOSITION THAT UNKNOWN DECAYED VEGETABLE ORGANIC MATERIALS HAVE ALREADY UNDERGONE IN NATURE[1]

GEORGE JOHN BOUYOUCOS

Michigan Agricultural Experiment Station

Received for publication December 29, 1933

Although there are methods (3) for following the process of decomposition of organic materials of known state, there is at present no method that can tell quantitatively how far an unknown decayed vegetable material has decomposed. For instance, we cannot take a sample of unknown muck and tell definitely how far this muck has decomposed from the parent material.

The development of the distillation method (1) for determining the amount of combined water and organic matter in soils indicated that the degree of decomposition of unknown decayed organic materials might be determined by the use of high temperature. Accordingly such a method has been developed. It is the object of this paper to present the method and the experimental results obtained through its use. This report is preliminary to a more complete investigation, which is being continued with special effort to perfect further the technique and apparatus.

EXPERIMENTAL

After considerable experimentation, the method finally adopted for determining the degree of decomposition of decayed organic materials is revealed in formulas (A) and (B).

$$\frac{\text{Per cent loss at 310°C. in a bomb}}{\text{Per cent loss on ignition at 550°C. in air}} = \text{Volatilization index} \qquad (A)$$

$$\frac{\text{Volatilization index of fresh material—Volatilization index of unknown decomposed material}}{\text{Volatilization index of fresh material}} \times 100 = \left\{\begin{array}{l}\text{per cent decomposition unknown decayed material has undergone in nature from fresh state}\end{array}\right. \qquad (B)$$

By dividing the per cent of volatile material by the per cent of total loss on ignition, any variation in the ash content of the different organic materials is taken into account. The final results, therefore, are not only comparable but also absolute for the various organic materials.

[1] Journal Article No. 177 (N. S.) from the Michigan Agricultural Experiment Station.

The procedure consists of allowing all the organic materials to become air-dry and grinding them to pass a 2-mm. mesh screen. Exactly 25 or 50 gm. of the air-dry material is placed in a bomb (1) and about 10 gm. in a crucible. The latter sample is used to determine the hygroscopic moisture and the ignition loss of the material. The lid is screwed on the bomb, and the joints are covered with a layer of asbestos cement to insure air-tightness. To take off the cement after heating in the furnace, the cap of the bomb is hit with a hammer and the cement breaks off readily. The process of putting on and taking off this asbestos cement is very simple and requires very little time. The bomb is now placed in an electric muffle at a temperature of 310°C. and allowed to remain for 24 hours. The bomb is then taken out of the muffle furnace and allowed to cool first in the air and finally in a large desiccator. After the bomb is completely cooled, its lid is taken off as described and its contents are poured into a previously weighed receptacle. To be sure that no foreign material will break off from the bomb while it is being emptied of its contents and thus contaminate the latter, cheesecloth is wrapped around the bomb. The contents are weighed on an analytical balance and the percentage of the original material which was volatilized at 310°C. for 24 hours is calculated on the oven-dry basis. To determine the loss on ignition, the material is first dried at 110°C. for 24 hours and then ignited in the muffle furnace at 550°C. for 12 hours. The percentage loss on ignition is then divided into the percentage loss at 310°C., which gives a certain factor or volatilization index for any one material, both in the fresh and decomposed state. Then the difference in the index between the fresh and decomposed state is divided by the index in the fresh state multiplied by 100 and the result is the extent of decomposition that the decayed material has undergone from its fresh state.

The procedure outlined gives very close checks if the temperature at which the materials are heated remains the same. Results show that the volatilization is very sensitive to temperature. If the temperature remains the same, checks will agree within 1 per cent. It is very essential, therefore, that the same temperature within 5°C. be maintained for all materials.

At the temperature of 310°C. the length of time of heating influences the amount of volatilization to a certain extent. Heating a material for 48 hours resulted in about 3 per cent greater loss than heating for 24 hours. At higher temperatures, such as 550°C., all volatilization at that temperature seems to be completed in much shorter periods. Heating the organic materials at higher temperatures such as 550°C. gives a higher volatilization index, but the relationship between the volatilization index of various materials is nearly the same as that which exists when the determinations are made at 310°C. The temperature of 310°C., however, seems to be the best temperature to heat the materials because it is nearer their critical temperature of decomposition, is not too drastic, and is also easier to maintain.

It is essential that the materials be heated in a bomb or in the absence of air, otherwise unequal heating due to premature ignition takes place.

In tables 1 and 2 are presented the experimental results on the volatilization index as obtained by the temperature method on a large number of different representative organic materials in the fresh and decomposed state. Unfortunately, it was very difficult to obtain very good samples of materials in a highly decomposed state other than muck. Nearly all the decayed materials

TABLE 1

Volatilization index of fresh materials heated at 310°C.

MATERIALS	HYGROSCOPIC MOISTURE	LOSS ON IGNITION	LOSS AT 310°C. IN BOMB	VOLATILIZATION INDEX
	per cent	*per cent*	*per cent*	*per cent*
Alfalfa stems	9.46	94.0	54.24	57.6
Alfalfa leaves	8.70	91.0	52.2	57.4
Clover, mature	13.35	94.22	51.11	54.58
Lettuce leaves, green	12.10	84.4	48.1	57.01
Oats, young plants	10.14	92.2	52.1	55.2
Oat straw	9.10	95.8	51.5	53.8
Wheat straw	7.7	96.2	55.18	56.4
Corn, mature stalks	5.8	92.58	53.51	57.6
Alfalfa roots	12.70	95.8	55.1	57.4
Pasture grass, green	9.93	91.80	49.0	53.4
Rye straw	9.80	96.15	51.4	53.4
Filter paper	4.15	99.95	55.94	55.95
Oakwood, sound	8.70	99.85	52.8	52.9
Pine wood, sound	8.66	99.80	53.0	53.05
Wheat flour	10.18	93.00	54.10	58.20
Sphagnum moss	10.20	92.0	47.8	51.9
Sedge	12.22	94.8	50.25	52.90
Wood shavings	8.84	99.5	53.2	53.5
Green water lilies	9.00	92.5	48.43	52.5
Horse manure	3.2	92.3	49.2	53.2
Cow manure	8.24	90.6	46.51	51.23
Oak leaves, mature	9.83	94.0	44.3	47.0
Maple leaves, mature	11.03	91.3	43.8	48.0
Beach leaves, mature	11.12	94.5	45.77	48.5
Pine needles, in fall	7.02	96.7	45.9	47.3
Walnut shells	8.08	99.3	54.8	55.2

were only partially decomposed, and their extent of decay was, of course unknown. In the Tables are also included the data on hygroscopic moisture, loss on ignition, and volatilization loss at 310°C.

Table 1, which contains the data for the fresh materials, shows that, with the exception of the tree leaves, the volatilization index of all fresh materials is not greatly different, ranging only from about 52 to 58 per cent. The most interesting thing is that such fresh materials as walnut shells, pine wood, and

oak wood have a volatilization index only slightly smaller than such fresh materials as alfalfa leaves, lettuce leaves, and wheat flour. The only fresh materials that seem to have decidedly different volatilization indexes from the rest of the fresh materials are the tree leaves. A possible explanation for this variation will be offered subsequently in this paper.

Table 2, which contains the results for the decayed or partially decayed organic materials, shows that their volatilization index varies from 0 to about 40 per cent, which is far below that of the fresh materials. With the exception of coal, mucks seem to have the smallest volatilization index, with the mini-

TABLE 2

Volatilization index of unknown decayed materials heated at 310°C.

MATERIALS	HYGROSCOPIC MOISTURE	LOSS ON IGNITION	LOSS AT 310°C. IN BOMB	VOLATILIZATION INDEX
	per cent	*per cent*	*per cent*	*per cent*
Wheat straw	9.09	84.0	30.5	36.3
Oat straw	9.22	81.2	29.7	36.6
Corn stalks	5.60	76.5	31.0	40.52
Clover	9.53	93.43	27.0	28.8
Wood 1	4.57	97.32	36.81	37.81
Wood 2	5.32	98.95	44.5	44.9
Sedge moss	11.25	95.36	34.2	36.0
Sphagnum moss	13.10	93.10	32.0	34.4
Beach leaves	10.32	60.00	23.36	38.93
Pine needles	13.38	82.20	33.2	40.82
Maple leaves	9.65	84.30	32.8	38.90
Horse manure	7.10	61.7	18.18	30.44
Cow manure	8.05	81.4	32.88	40.4
Raw peat 1	9.42	97.2	38.5	39.6
Raw peat 2	8.32	97.12	37.7	38.8
Peat	12.23	97.90	26.00	33.4
Muck 1	12.47	90.0	20.9	23.3
Muck 2	12.87	79.10	21.78	27.55
Muck 3	11.05	79.8	22.7	28.7
Muck 4	13.15	88.7	20.20	22.8
Pocahontas Coal	0.58	97.5	0.0	0.0

mum around 23 per cent. Peats have a higher volatilization index, with a maximum around 38 per cent.

What is the meaning of the difference in the volatilization indexes between the fresh and decayed organic materials as revealed in tables 1 and 2? The higher volatilization index of the fresh materials over that of the decayed materials simply means that the fresh materials have a high content of easily decomposable substances which are volatilized at the temperature of 310°C., while the decayed materials have a low volatilization index because their easily decomposable substances have already disappeared in the natural de-

composition process and there is left behind a higher content of the resistant substances.

The lower volatilization index of the fresh but mature leaves of trees might be explained somewhat on the same basis as that of decayed materials. Since the leaves serve the purpose of manufacturing the food of the trees, their easily decomposable substances, such as the sugar, are taken away from them by the trees, and as a consequence their composition contains a correspondingly greater proportion of the more resistant substances such as lignin.

TABLE 3

Degree of decomposition unknown decayed materials have already undergone in nature from their original fresh state

MATERIALS	VOLATILIZATION INDEX OF FRESH MATERIAL	VOLATILIZATION INDEX OF DECAYED MATERIAL	DIFFERENCES BETWEEN FRESH AND DECAYED MATERIAL	DEGREE OF DECOMPOSITION DECAYED MATERIALS HAVE UNDERGONE FROM FRESH STATE
	per cent	*per cent*	*per cent*	*per cent*
Wheat straw	56.4	36.3	20.1	35.6
Oat straw	53.8	36.6	17.2	32.0
Corn stalks	57.6	40.5	17.1	29.7
Clover	54.6	28.8	25.8	47.3
Wood	52.9	37.8	15.1	28.5
Sedge moss	52.9	36.0	16.9	31.9
Sphagnum moss	51.9	34.4	17.5	33.7
Beech leaves	48.5	38.9	9.6	19.8
Pine needles	47.3	40.8	6.5	13.7
Maple leaves	48.5	38.9	9.6	19.8
Horse manure	53.2	30.4	22.8	42.9
Cow manure	51.2	40.4	10.8	21.1
Raw peat	53.0*	39.6	13.4	25.3
Muck 1	53.0*	22.8	30.2	57.0
Muck 2	53.0*	27.5	25.5	48.1

* In fresh state.

The products formed both by the destructive distillation at 310°C. and by aerobic fermentation seem to be qualitatively similar; namely, water, carbon dioxide, and ammonia. It remains to be determined whether they are also quantitatively similar. The residual products, such as lignin, also seem to be similar under the two processes.

The data in table 3 reveal a very wide difference in the degree of decomposition that the various unknown decayed organic substances have already undergone from their fresh state. They show for instance that the decayed sample of pine needles used had decayed only 13.7 per cent from the original state, whereas muck had decayed 57 per cent from the fresh parent material. These measurements were obtained according to the formulas already presented.

How closely the indicated degree of decomposition represents the real decomposition that has actually taken place in nature in the various decayed materials cannot, of course, be stated, as there is no way of knowing. The results, however, seem to be reasonable.

SUMMARY

A method, based on volatilization, is presented for determining the degree of decomposition that unknown decayed vegetable organic materials have already undergone in nature from their fresh state.

The method consists of heating the materials in a bomb at 310°C. for 24 hours. The volatilization loss that takes place at this temperature is divided by the ignition loss of the material, and that gives a certain volatilization index.

It is found that the volatilization index of fresh materials is much higher than that of the decayed materials.

It is assumed that this difference in the volatilization index represents degree of decomposition of the decayed materials. When the volatilization index of a certain material in both the fresh and the decayed states is known, the degree of decomposition that the decayed material has already undergone can be ascertained.

By this method it is shown, for instance, that some mucks have already undergone a decomposition of 57 per cent from the original state.

REFERENCES

(1) BOUYOUCOS, G. J. 1932 A method for determining combined water and organic matter in soils. *Soil Sci.* 34: 259–265.

(2) HURD, CHAS. D. 1929 The Pyrolysis of Carbon Compounds. The Chemical Catalog Company, New York.

(3) WAKSMAN, S. A. 1932 Principles of Soil Microbiology. The Williams & Wilkins Company, Baltimore.

MORPHOLOGY AND GENESIS OF THE SOLONETZ SOILS OF WESTERN NORTH DAKOTA

CHARLES E. KELLOGG[1]

North Dakota Agricultural College

Received for publication January 26, 1934

The prominent feature of the solonetz soils is the presence of sodium among their exchangeable bases. According to the work of K. K. Gedroiz the solonetz soils represent one stage in the evolution of the alkali soils (3). These genetic stages in the evolution of such soils may be summarized as follows:[2]

(*a*) Normal soil (chernozem, brown soil, etc.). In these soils the base exchange is largely saturated with the divalent cations, the colloids are in a flocculated state, and the soil is nearly neutral. The *calcification* process is dominant.

(*b*) Solonchak (saline). In this case there is an excess of soluble salts and usually some portion of the divalent cations have been replaced by monovalent cations, especially sodium. The presence of the excess salts prevents the hydrolysis of the sodium from the exchange and keep the colloids flocculated. The soil is not highly alkaline.[3] This process is best called *salinization.*

(*c*) Solonetz (alkali soil). These soils have a relatively high percentage of exchangeable sodium in the complex and a low percentage of soluble salts. As the drainage of the solonchak becomes improved the excess soluble salts are removed. In such cases where these salts were essentially all divalent the soil changes back to the normal. In most instances, however, the solonchak contains a considerable amount of exchange sodium, such that when the excess salts are removed the colloids are given an increased mobility and the soil becomes highly alkaline as a result of the hydrolysis of the sodium to form sodium hydroxide. (This, of course, passes to sodium carbonate.) Because of the deflocculated state of the colloidal portion, the soil exhibits a prismatic structure with hard aggregates. This process is called *solonization* and might be said to consist of desalinization plus alkalinization.

(*d*) Soloth. As soon as solonetz has formed, the highly dispersed colloids tend to move downward in the solum. In a sense this process is similar to podzolization except that the original mobility of the colloids is due to exchange sodium rather than to exchange hydrogen. The exchange capacity of the soil becomes reduced and the pH becomes lower with an increase in exchangeable hydrogen. A light colored A_2 horizon with a platy structure and a light texture develops over a dark, hard, columnar B_2 horizon. With the completion of the development the B_2 horizon loses its columnar structure and itself becomes somewhat acid. This process is called *solodization.*[4]

[1] Now with the Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

[2] Nikiforoff, C. C. Evolution of the alkali soils; their classification and reclamation. Unpublished manuscript.

[3] Except in the unusual case of flooding with sodium carbonate which has been introduced from a solonetz at a higher level.

[4] This process has been spoken of as the "degradation of the solonetz" but the writer feels that the term "degradation" should be confined to the influence of the podzolization process.

(*e*) Normal soil (chernozem, brown soil, etc.). After the complete formation of soloth with the removal of the mobile colloids, the continued growth of the native grasses again changes the soil to that normal for the region. This process of calcification impinged on the soloth might be called *reconstruction.*

The most common occurrence of the solonchak, and consequently the solonetz and soloth, is as a "complex." Within an area having the normal profile, or nearly such a profile, will be irregular spots of these soils. And these spots will not be uniform in any characteristic. Kelley has presented some interesting data on the irregular nature of alkali soils in California (4). In soil mapping such areas must be classified simply as a complex.

Differences in the solonchak stage will, of course, be reflected in both the solonetz and the soloth. The solonchak may have almost any conceivable ratio of the various cations in the saline waters: hence, depending upon the ratio of divalent to monovalent cations, the resulting solonetz will vary all the way from the normal profile, through a weak solonetz profile, to the extremely hard, prismatic solonetz. These salts may have drenched the soil quite uniformly from the surface, as in a level lake floor, or, as is more generally the case, have risen in irregular patches from the water table. Again the salts, having risen by capillary action with the water, may come to the surface and gives rise to a crust of *puff* at the surface (exterior solonchak), or the capillary movement may have ceased at some depth within the profile, leaving the salts beneath the surface (interior solonchak).

As a further complication, all stages of development between solonchak and soloth may be found. As a matter of fact, one rarely, if ever, finds a solonetz which is not tending either somewhat toward solonchak or toward soloth. As soon as solonetz forms it immediately begins to solotize with the development of a profile approaching the soloth.

SOLONETZ SOILS OF WESTERN NORTH DAKOTA

During the summer of 1931 and subsequently the writer has been much interested in the solonetz-complex of western North Dakota. Large areas in the Great Plains, and extending north into Canada, are characterized by a spotted appearance of the surface. Small, irregular, but roughly elliptical, depressions break the uniformity of the prairie landscape. Such a landscape is perhaps best summarized in the words of Dokuchaev as "smallpox on the face of the steppe" (7). These depressions are usually about 6 to 15 inches in depth and 4 to 15 feet in diameter. They are either barren of vegetation or support a meager growth of xerophytic and halophytic plants. Locally these spots are known as "buffalo wallows" or "slick spots;" and in Canada as "burnouts" (6). When the land is plowed they are evident by their hard, cloddy nature when dry and by extreme stickness when moist.

The solonetz-complex is found on nearly level or gently sloping land, and is developed from a variety of parent materials including glacial till, weathered sandstones and shales, and alluvial deposits. In cases where this condition

is developed from glacial till, the till is thin over the weathered marine deposits or the till takes the form of a gentle slope away from some higher outcrop of the residual material, the seepage from which may influence the soil on the slope.

GENERAL FEATURES OF THE AREA

The climate is of the extreme continental type with hot summers and cold winters. The annual rainfall varies considerably from a yearly mean of about 15 inches. The general features of importance are shown in figure 1.

The parent material for soil of the northern part is of glacial origin, underlain by marine deposits of sandstone, shale, and clay. In the southern part of western North Dakota the soils are developed directly from this residual

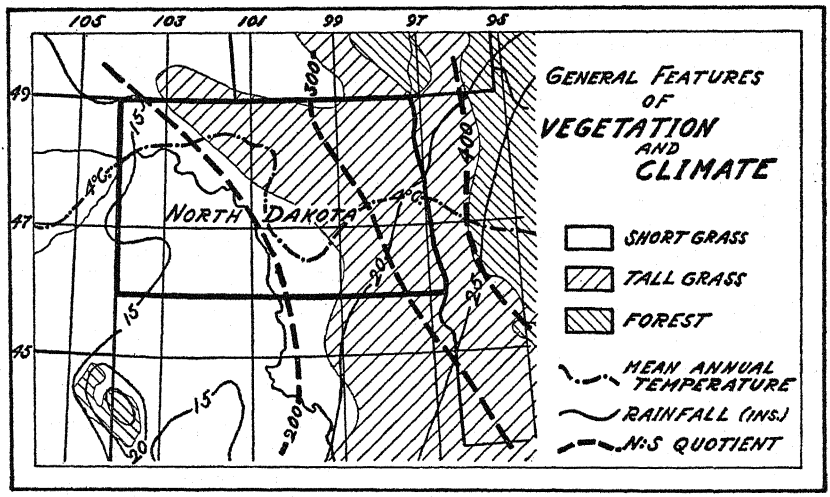


FIG. 1. SKETCH MAP SHOWING THE GENERAL FEATURES OF VEGETATION AND CLIMATE FOR WESTERN NORTH DAKOTA

material. The clayey alluvium of the slopes and valleys frequently gives rise to the solonetz-complex.

The native vegetation consists of the mixed prairie type with such species predominating as grama grass (*Bouteloua gracilis*), needle grasses (*Stipa comata and Stipa viridula*), nigger wool (*Carex filifolia*), June grass (*Koeleria cristata*), western wheat grass (*Agropyron smithii*), and salt grass (*Distichlis spicata*). This last named species is found only on the solonchak and solonetz soils together with salt sage (*Atriplex nuttallii*), cacti (*Opuntia fragilis*), and similar plants.

The normal soil for the area varies from the chestnut brown soils in the neighborhood of the Missouri River at Bismarck to the brown soil near the Montana state line. On the steeper, and consequently drier, slopes sierozems (gray soils) are developed. Many large areas show some definite influence

from sodium but are not sufficiently solonized to be classified as solonetz, although there is a pronounced prismatic structure and a dark brownish-gray color. The dominant profile for the western part of the area is shown in figure 2 and may be illustrated by the profile from Scobey loam, described a little later.

INVESTIGATIONS

This investigation has fallen naturally into two parts: (*a*) The field study of the morphology of the soils, together with observation of the vegetation, relief, and other factors of importance in genesis. Clearly this is the most important phase of a study of this kind. After the examination of a great

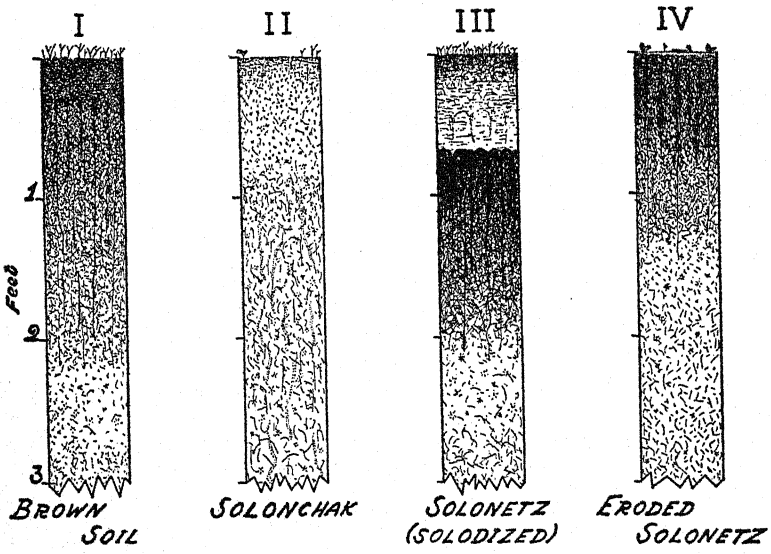


FIG. 2. SKETCHES SHOWING SOME OF THE PRINCIPAL TYPES OF PROFILES MENTIONED IN THE TEXT

many profiles they were classified according to their development, and examples are presented which most nearly approach the average for each class. (*b*) A few laboratory determinations were made in order to throw further light on the more detailed conditions in the soil horizons.

For such an investigation a great many morphological studies were made from excavations in what appeared to be different stages in the development. From a portion of these profiles, samples were collected by horizons for physical and chemical determinations.[5]

Profile descriptions were made in accordance with the uniform method described in detail previously (5).

[5] The writer has been assisted by his students and by workers in the U. S. Bureau of Chemistry and Soils in making the laboratory determinations.

Depression of the freezing point (-d F. P.) has been determined as a measure of the soluble material in the soil according to the general method of Bouyoucos and McCool (2), except that the soil and water are in the ratio of 1:1.

pH was determined in the regular way by use of the hydrogen-electrode. In this case the ratio of soil to water was 1:2½.

Mechanical analysis was determined in all cases, except for the normal profile, by use of the hydrometer method as suggested by Bouyoucos (1) and modified in the Bureau of Public Roads (8, 9).

For the extraction of the exchangeable material in the soil, 20 gm. of soil was treated with 100 cc. of 0.05 *N* HCl plus the HCl-equivalent of carbonates present. Three successive treatments with 50 cc. of HCl were likewise made and filtered, and the material obtained was combined and analyzed. This was followed by a sufficient number of treatments with 50-cc. portions until the residual dry matter amounted to only 5 to 10 mgm. The residues from all these filtrations were combined and analyzed. In table 4, giving the results for solonschak, only a total of 250 cc. of HCl was used.

The Normal Soil

The normal soil for the western part of the area may be illustrated by the following profile from the Scobey loam (see also fig. 2):

*Scobey loam (profile 1)**

A_1†	0 to 1″	Dark grayish brown light loam with soft, fine crumb, mulch-like structure. Thoroughly permeated with roots.
A_2	1 to 4½″	Dark brown loam with soft crumb structure. In place, the soil is fairly platy. The lower part of the horizon grades into the prisms of B_2. This portion of the soil contains many grass roots.
B_2	4½ to 13″	Brown (faintly reddish) sandy clay loam with a very well-developed prismatic structure. These vertical prismatic blocks range from ½ to 1½ inches in diameter. When removed the soil is in vesicular, elongated pieces ranging from small to large nut-size, and held together by grass roots. These pieces are fairly easily crushed to a medium hard crumb. When dry the prisms are noticeably brittle. This layer grades into
B_3	13 to 20″	Brown, with olive-drab tinge, sandy clay loam. The soil has a well-developed prismatic structure, but the vertical prisms and their constituent blocks are somewhat larger than those in B_2 and somewhat less friable. The soil effervesces very mildly with HCl. Roots penetrate the solum with ease, but few go beneath this horizon.
C_1 (Carbonate)	20 to 26″	Light olive-drab, strongly mottled with white, sandy clay till. The soil is compact in place, but removed chunks are easily friable. In the lower part the mottling becomes less intense and the soil grades into
C	26″	Light olive-drab sandy clay till.

* Location: SW¼. SW¼. Section 7, T151N, R100W.

† Horizon nomenclature throughout this paper is according to the method outlined elsewhere (5).

TABLE 1

*Mechanical analysis of Scobey loam, profile 1**

HORIZON	DEPTH	FINE GRAVEL	COARSE SAND	MEDIUM SAND	FINE SAND	VERY FINE SAND	SILT	CLAY	TOTAL	COLLOID	ORGANIC MATTER BY H_2O_2
	inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A_1	0–1	0.6	3.1	6.2	17.2	9.1	37.7	21.0	94.9	16.0	4.6
A_2	1–4½	0.9	3.4	6.8	19.1	9.8	35.2	21.3	96.5	18.4	3.1
B_2	4½–13	0.4	3.2	6.8	20.0	9.8	27.2	30.4	97.8	26.0	1.9
B_3	13–20	0.8	2.6	6.0	15.8	10.2	26.8	36.5	98.8	30.3	1.0
C_1	20–26	0.9	2.2	3.9	10.5	10.0	26.7	44.7	98.9	34.2	0.8
C_2	26+	1.5	2.2	3.7	10.5	10.9	29.8	40.6	99.2	32.2	0.3

* By H. W. Lakin and T. M. Shaw.

TABLE 2

*Total chemical analyses of Scobey loam, profile 1**

HORIZON	DEPTH	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	IGNITION LOSS	TOTAL	N	ORGANIC MATTER COMBUSTION METHOD	pH	−d F·P
	inches	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		°C.
A_1	0–1	74.26	0.48	10.84	2.78	0.08	1.43	0.82	2.03	1.11	0.21	0.15	6.71	100.90	0.23	3.71	6.4	0.010
A_2	1–4½	72.66	0.54	12.54	3.09	0.07	1.14	0.78	2.12	1.19	0.16	0.12	5.40	99.81	0.16	2.50	6.3	0.014
B_2	4½–13	73.38	0.54	12.41	3.77	0.06	1.29	1.14	2.10	1.08	0.15	0.11	4.01	100.04	0.10	0.99	6.7	0.004
B_3	13–20	68.14	0.58	13.09	4.52	0.07	2.32	1.69	2.02	0.97	0.22	0.12	6.00	100.74	0.10	1.42	6.85	0.007
C_1	20–26	57.44	0.49	11.38	4.10	0.06	9.77	2.64	1.79	0.91	0.23	0.12	11.89	100.82	0.10	1.32	7.85	0.014
C	26+	58.19	0.56	12.90	4.30	0.07	8.44	3.25	1.99	1.07	0.25	0.14	9.52	100.68	0.04	1.46	7.95	0.010

* Chemical analyses by Mr. G. J. Hough of the Bureau of Chemistry and Soils.

The mechanical and chemical analyses of this profile are shown in tables 1 and 2 respectively. These data show that there likely has been some movement of colloid from the upper to the lower part of the solum.

The Solonchak Stage

Throughout the region under discussion are areas of solonchak, but these are much less numerous at present than the areas of the solonetz-complex. Two profiles from those investigated are herein presented as typical of the solonchak—complex. In figure 3 is shown a cross section made through one of the puffed spots. The most striking feature of such soils is the puffing at the surface in small, irregular spots. In cases where the salty water moves up by capillary action from the water table, as soon as the salt comes in contact with the clay the colloids will become flocculated and capillary activity intensified.

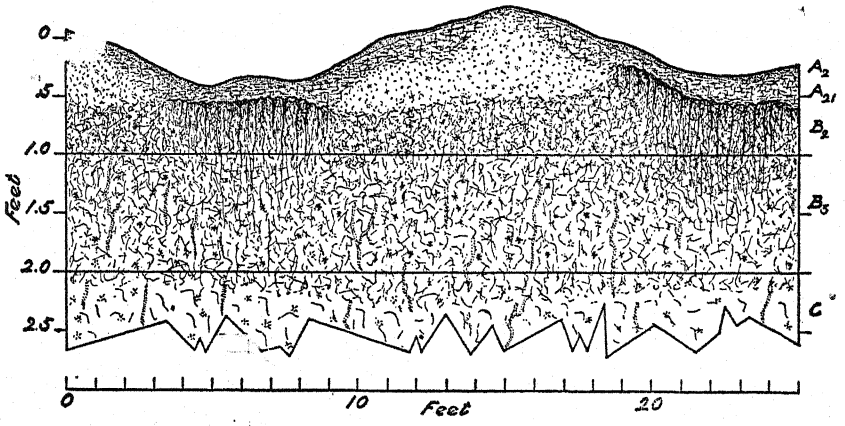


FIG. 3. CROSS SECTION, MADE TO SCALE FROM LEVEL NOTES, THROUGH THE PUFFED SPOT IN THE SOLONCHAK-COMPLEX

Three profiles included in this section are described

In this way any small inequalities in the original material become greatly intensified. Likely one could never expect to find an area of solonchak in which the salts have risen from beneath that would be at all uniform. It is important to note here that the general feature of discontinuity characteristic of most alkali soils in all stages is introduced during the earliest stage of their evolution. These raised, or puffed, spots cover roughly one-half of the area. A picture of this type of landscape is reproduced in plate 1, figure 1.

The profile described in the following is taken through the puffed spot shown in the cross section of figure 3. The soil is developed from alluvium on a stream terrace. The terrace has about 1 per cent of slope toward the stream and away from the adjacent upland. The vegetation on the puffed spots consists of a sparse stand of salt grass, salt sage, Texas crab grass, and

Russian thistle. Between the spots the vegetation is somewhat more dense and includes western wheat grass and a little grama grass.

*Solonchak (profile 3)**

A_2	0 to $\frac{1}{4}''$	Light gray, light very fine sandy loam. This brittle, vesicular crust is easily crushed to a single grain structure.
A_{21}	$\frac{1}{4}''$ to 2″	Light grayish brown, heavy very fine sandy loam. With difficulty the soil rubs to nearly a single grain. There are a few irregular vertical cracks.
B_1	2 to 9″	Light brown fine sandy clay with a very fluffy, fine crumb structure. When dry many small crystals of salt may be seen.
B_2	9 to 14″	Brownish olive clay with a soft crumb structure, containing noticeable white flecks.
B_3	14 to 30″	Light brownish olive clay, containing many white flecks. The material is soft and friable (flocculated) in place but squeezes into a cheesy mass.
C	30″	Heavy olive clay, massive and plastic in place, but not hard, and contains many white flecks.

* Location: E½, Section 17, T150N, R98W.

Another profile, taken at the margin of the puffed space may be described as follows:

Profile 4

A_2	0 to $\frac{1}{2}''$	Gray, light very fine sandy loam. This brittle, vesicular crust is easily crushed to a single grain structure.
A_{21}	$\frac{1}{2}$ to 1″	Brownish gray, heavy very fine sandy loam. A few irregular vertical cracks appear, although the soil is somewhat platy. Pieces are hard and brittle and are rubbed to a single grain with difficulty.
A_{22}	1 to 3″	Light brown fine sandy clay loam with some platiness. The soil is brittle but easily friable to a medium crumb. White flecks appear in the lower part.
		The remainder of the profile is similar to profile 3.

Profile 5

A_2	0 to 1″	Gray fine sandy loam. The soil is brittle and platy but contains more organic matter than the surface layers of the profiles described above.
A_{21}	1 to 3″	Yellowish-brown platy, brittle heavy loam.
B_2	3 to 8″	Dull brown clay with ill-defined prismatic structure. The prisms are hard and finely vesicular; they are crushed with difficulty to angular pea-sized pieces.
B_3	8 to 20″	Light brownish olive clay with a few vertical cracks. The mass has a soft, subangular, pea-sized structure.
		There are many flecks and vertical streaks of salt.
		The remainder of the profile is similar to that described under profile 3.

Table 3 gives data regarding the physical nature of this soil, and table 4 gives data regarding the chemical nature of the material extracted with dilute

HCl. These data clearly show a solonchak which is just beginning to develop into a solonetz. The salts have already left the very upper layers, and the

TABLE 3

Mechanical analyses, pH, and $-d\,F{\cdot}P$ of solonchak, profiles 3, 4, and 5

PROFILE NO.	HORIZON	DEPTH	MECHANICAL ANALYSIS*				$-d\,F{\cdot}P$†	pH‡
			Sand above 0.05 mm.	Silt 0.005 to 0.05 mm.	Clay below 0.005 mm.	Fine clay below 0.002 mm.		
		inches	*per cent*	*per cent*	*per cent*	*per cent*	°C.	
3	A_2	0–¼	..	..	..	..	0.039	8.9
	A_{21}	¼–2	..	..	..	..	0.012	9.05
	B_1	2–9	37	33	30	18	0.466	9.1
	B_2	9–14	31	34	35	25	0.510	9.1
	B_3	14–30	27	36	37	27	0.504	9.3
	C	30+	29	42	29	21	0.471	9.15
4	A_2	0–½	43	47	10	7	0.022	8.8
	A_{21}	½–1	47	33	20	14	0.044	9.3
	A_{22}	1–3	..	..	..	..	0.233	8.75
5	A_2	0–1	40	39	21	15	0.002	8.1
	A_{21}	1–3	35	42	23	16	0.020	8.0
	B_2	3–8	36	33	31	24.5	0.057	9.4
	B_3	8–20	25.5	30.5	44	34	0.320	9.05

* By the hydrometer method, as modified in the Bureau of Public Roads (8, 9).
† For the depression of the freezing point, ratio of soil and water, 1:1.
‡ By the hydrogen electrode.

TABLE 4

Exchange material extracted from solonchak, profiles 3 and 4 by treatment with 0.05 N HCl*†

(m.e. per 100 gm. soil)

HORIZON	PROFILE NO.	DEPTH	SiO_2	Al_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TOTAL
		inches								
A_2 (crust)	3	0–¼	1.36	5.94	0.25	22.95	16.90	0.25	1.51	49.16
A_{21}		¼–2	1.86	4.71	0.25	20.80	18.60	0.24	3.83	50.29
B_1		2–9	1.19	3.88	0.17	45.50	16.30	0.24	11.00	78.28
A_2 (crust)	4	0–½	1.42	5.12	0.29	23.92	17.10	0.25	1.16	49.26
A_{21}		½–1	1.32	4.12	0.25	23.10	17.80	0.30	3.26	50.15
A_{22}		1–3	1.20	2.18	0.22	43.00	11.55	0.35	5.71	64.21
B_1		3–6	(As B_1 in profile above)							

* Analyses by G. H. Hough.
† Extraction with only 250 ml. 0.05 *N* HCl.

sodium saturated colloids in those layers have produced enough NaOH to raise the pH of the soil to about 9. Also the colloids have begun to move out of the upper layers and become flocculated beneath. It is interesting to note

that the major profile, number 3, has already started to solodize even before the development of a true A_1 horizon and while the soil as a whole is much more nearly a solonchak than a solonetz, from a morphological standpoint at least.

A few areas of rather uniform solonchak of the flooded type are to be found. These are developed in old ponded areas and usually from parent materials of heavy clay, either of lacustrine or alluvial origin. The following profile may be taken as typical of such solonchak:

*Solonchak (profile 6)**

A_1	0 to 1½″	Light gray fine sandy clay. This material is essentially a porous, brittle crust, friable with some difficulty to a dust.
A_2	1½ to 6″	Gray clay, fairly friable.
C	6″	Dark olive-gray clay, noticeably hard when dry but friable at ordinary moisture contents, grading in depth to friable material somewhat more grayish in color. There are numerous flecks of salt.

* Location: Section 17, T149N, R99W.

The vegetation on this soil consists chiefly of sage brush (*Artemisia cana*) and a scanty growth of salt grass, prostrate spurge (*Euphorbia glyptosperma*), and similar plants.

When such a soil develops into a solonetz it will obviously produce one of more uniform character than the puff solonchak.

The Second and Third Stages: The Solonetz-Complex

Of the hundreds of solonetz profiles examined by the writer, every one showed at least some solodization.

The following profile, developed from material laid down in an old ponded area, has very little solodization and the soil of the area is more nearly uniform in character than is usually the case. The native vegetation consists largely of western wheat grass.

*McKenzie clay, Solonetz (profile 7)**

A_1	0 to 1½″	Dark grayish brown clay loam, thoroughly permeated with roots.
A_2	1½ to 3″	Very dark grayish brown clay with a hard, coarsely granular structure.
B_2	3 to 14″	Brownish black clay with a very hard, prismatic structure. These prisms vary from 1 to 6 inches in diameter and break with difficulty into irregular, sharply angular pieces. In the upper part the soil is faintly mottled with rusty brown.
B_3	14 to 24″	Very dark gray clay. The prisms become much less distinct and the soil more massive.
C	24″—	Very dark gray massive clay. The soil digs out in large, massive chunks with difficulty. Only a few vertical cracks extend into this material.
		Large cracks extend from the surface down into the soil and into

these the surface soil falls, bringing about some mechanical mixing of the soil. The soil reacts with HCl only below 30 inches.

* Location: Section 30, T150N, R99W.

Profile 7 is not well developed, likely because of its youth and the extreme nature of the parent material. The soil must be classified as a solonetz developed from the flooded type of solonchak described under profile 6.

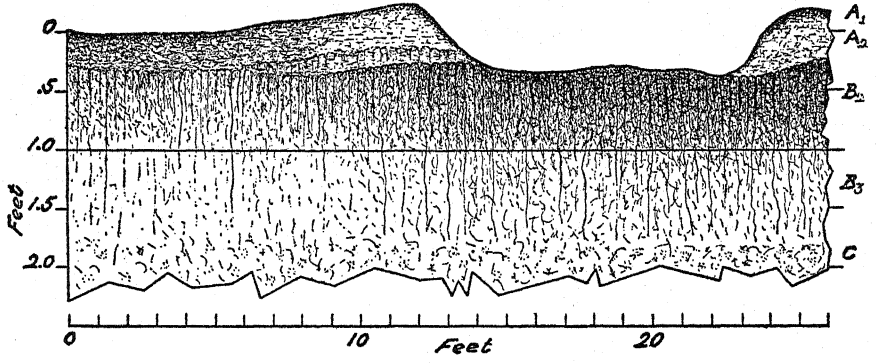


FIG. 4a

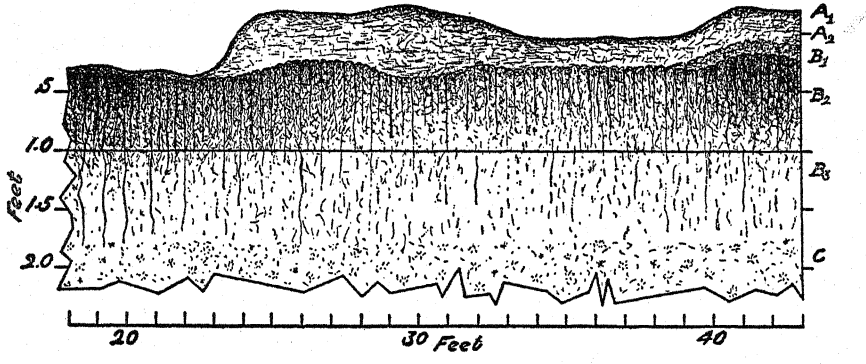


FIG. 4b

FIG. 4. CROSS SECTION, MADE TO SCALE FROM LEVEL NOTES, THROUGH AN ERODED SPOT ON THE SOLONETZ-COMPLEX

The two drawings overlap. Note that at the right of the section there is an old depression, now covered with buffalo grass and on the way toward reconstruction. In the freshly eroded spot note that the eluviated surface soil has been removed, exposing the heavy, intractable clay of the B horizon. Obviously a part of this fine material has been removed by wind just to the margin.

But by far the most common type of solonetz is the solonetz-complex. This complex may be associated with any one of a great variety of soil types, such as those developed from glacial till, from residual material, or from either local or general alluvium. In figures 4a and 4b is shown a cross section through an

eroded solodized solonetz spot occurring in a brown soil developed from glacial till. At the extreme right in the drawing is shown an old spot, now grassed over with buffalo grass (*Bulbilis dactyloides*), and in the stage of reconstruction back to the normal profile. This drawing was made to scale from an actual excavation in place. The profile just a few inches back from the margin of the eroded spot may be described as follows:

*Solodized solonetz (profile 8)**

A_1	0 to 1″	Brownish gray loam with a soft crumb or mulch-like structure.
A_2	1 to 3″	Grayish brown loam with a platy structure that is easily friable.
B_1	3 to 5″	Dull grayish brown silt loam. The soil shows relicts of an old prismatic structure but is distinctly platy. The material is rather easily friable to a medium crumb structure.
B_2	5 to 8″	Dark brown clay with a well-developed, hard columnar structure. The caps of the columns are well developed.
B_3	8 to 12″	Olive-brown clay with irregular prismatic structure. The soil very easily crumbles into subangular, nut-sized pieces that are friable with difficulty.
B_{31}	12 to 22″	Olive-brown clay similar to the above except that carbonates are present and there are numerous white flecks and streaks.
C_1	22 to 26″	Olive-gray sandy clay, highly mottled with white. This material is compact in place and digs out in brittle, rather easily friable pieces.
C	26″—	Olive-gray sandy clay till, mottled with white. The material is compact in place and digs out in brittle, rather easily friable pieces, but when these pieces are dry they become very hard.

* Location: Section 23, T150N, R100W.

Table 5 and 6 show that profile 9 obviously represents a more advanced stage than does profile 8. It is to be noted, in passing, that the content of extractable sodium is especially high in the A_1 horizon, showing its constant return to the surface.

Such a soil easily erodes by wind and water if once a start is made in the surface. The lighter textured, friable surface soil becomes removed, leaving exposed the dark, hard clay of the B horizon. Such a clay spot is shown in the cross section of figure 4. It is interesting to note that the puffed region in the solonchak-complex becomes the depressed area in the solonetz-complex. The native vegetation on the soils, as previously described, consists largely of grama grass with some other species, such as western wheat grass and needle grass. But in the eroded spot the first vegetation to come consists of such plants as cacti, especially *Opuntia fragilis*, salt grass, and salt sage. These plants are followed by western wheat grass and finally by buffalo grass. It is interesting to note that in this region, which is near the northern limit for buffalo grass, the majority of the stands of that grass are limited to these old eroded spots in the solonetz-complex.

As soon as the vegetation has again become established, surface soil horizons

begin to form from the old, exposed B horizon of the solodized solonetz. The profile through such a stage is described as follows.

*Reconstruction of eroded solodized solonetz (profile 10)**

A_1	0 to 1″	Grayish brown loam with a soft crumb or mulch-like structure.
A_2	1 to 2½″	Brownish gray friable loam.

TABLE 5

Mechanical analysis, pH, and $-d\,F\cdot P$ of solidized solenetz of the solonetz-complex, profiles 8 and 9

PROFILE	HORIZON	DEPTH	MECHANICAL ANALYSIS				$-d\,F\cdot P$	pH
			Sand above 0.05 mm.	Silt 0.005 to 0.05 mm.	Clay below 0.005 mm.	Clay below 0.002 mm.		
		inches	*per cent*	*per cent*	*per cent*	*per cent*	*°C.*	
8	A_1	0–1	42	40	18	10	0.015	7.6
	A_2	1–3	44	36	20	15	0.011	7.3
	B_1	3–5	40	36	24	16.5	0.015	7.35
	B_2	5–8	52	26	22	18	0.026	8.05
	B_3	8–12	38	19	43	35.5	0.076	8.6
	B_{31}	12–22	33	24.5	42.5	31	0.137	8.1
	C_1	22–26	61.5	16	22.5	17	0.130	9.25
	C	26+	68.5	15.5	16	12.5	0.139	9.35
Surface of the eroded spot		0–2	32	36.5	31.5	24	0.032	8.15
9	A_1	0–½	40	49	11	7.5	0.010	7.35
	A_2	½–5½	..	..	..	..	0.025	6.75
	B_1	5½–8	..	..	..	..	0.027	6.86
	B_2	8–12	37	37	26	19	0.021	7.1
	B_3	12–25	26	45	29	25.5	0.070	8.2
	C	25+	31	40.5	28.5	24	0.090	7.35

TABLE 6

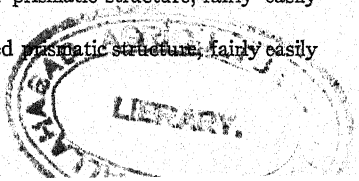
*Exchange material extracted from solodized solonetz, profile 9** *by treatment with 0.05 N HCl*

(m.e. per 100 gm. soil)

HORIZON	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TOTAL
	inches									
A_1	0–½	6.17	10.52	2.32	0.67	22.42	9.05	0.95	5.60	57.70
A_2	½–5½	5.44	9.03	2.31	0.56	22.52	6.97	0.98	2.59	50.40
B_1	5½–8	4.61	13.70	1.95	0.83	23.11	6.70	0.95	2.17	54.02
B_2	8–12	5.91	14.87	2.17	0.91	22.40	5.92	0.79	2.99	55.96
B_3	12–25	9.24	15.99	3.99	0.64	19.35	11.24	0.88	4.60	66.13
C	25+	8.93	19.85	4.80	0.24	21.58	9.70	1.14	7.18	72.42

* Analyses by G. J. Hough.

B_2	2½ to 9″	Dark brown clay with ill-defined prismatic structure, fairly easily friable to a medium crumb.
B_3	9 to 20″	Brownish olive clay with ill-defined prismatic structure, fairly easily friable.



The lower part of this profile is similar to that described under profile 8.

*Location: Adjacent to profile 8. This profile was taken through the old depression shown at the left in the cross section given in figure 4.

A great many variations in profile character are to be found in the solonetz-complex. On the one hand is the normal soil and at the other extreme is the solonetz developed from the flooded type of solonchak. When this latter type solodizes the A_2 horizon becomes strongly eluviated, as shown in the following description of profile 11. All gradations between may be observed. It would seem that in extreme cases of saturation with sodium salts during the solonchak stage the resulting solodized solonetz has a sharper profile: the horizons are more pronounced in their characteristics and the division between A and B is abrupt. Where the solonchak contains a smaller proportion of sodium, as compared to the divalent cations, the A horizon is less strongly eluviated and there are wide transitional horizons. These transitional layers show relicts of the old columnar structure as well as the characteristic platiness. Further, it may be that the type of vegetation which follows the solonchak is important. Plants which take in large amounts of sodium through their roots would tend to intensify the solodization process in the soil as compared to plants containing a smaller amount of this element.

In the case of solodization of the solonetz (profile 7) developed from the flooded type of solonchak (profile 6) the area is more uniform in original surface feature and in profile character. Such a soil does not exhibit the pronounced micro-relief characteristic of the solonetz-complex; there seems to be no differential erosion.

*Solodized-solonetz from flooded Solonchak (profile 11)**

A_1	0 to $\frac{3}{8}$″	Dark grayish brown very fine sandy loam.
A_2	$\frac{3}{8}$ to $4\frac{1}{2}$″	Brownish gray silt loam with well-developed platy structure, very friable and mellow.
A_{21}	$4\frac{1}{2}$ to 9″	Gray silty clay loam with well-developed, friable, platy structure. Some relicts of old columnar structure.
B_2	9 to 15″	Very dark brown clay with heavy, massive columns 2 to 4 inches in diameter. The soil breaks with difficulty into angular nut-sized fragments.
B_3	15 to 23″	Dark olive-brown clay with massive, poorly developed prismatic structure.
C_1	23 to 30″	Olive-gray, mottle with white, compact, friable clay.
C	30″	Olive-gray, friable clay, less strongly mottled with white than the above.

*Location: SW$\frac{1}{4}$. SW$\frac{1}{4}$. Section 35, T149N, R95W.

This profile represents the most advanced stage of solodization found by the writer in the entire area. The present vegetation on the soil consists of western wheat grass, grama grass, and similar species. The xerophytic and halophytic

plants, typical of the solonetz, have been entirely displaced by an association of plants very like that found on the normal soil. Unfortunately samples sufficient for mechanical analyses are not available. In table 7 are given the results for the depression of the freezing point and for pH. These values would indicate the soil to be rather close to a true soloth. In table 8 are shown the analyses of the HCl-extracts. Here it is noted that the calcium has greatly increased in the A_1 horizon but that the sodium has not. From these data, together with the morphology, it is evident that this profile is undergoing reconstruction.

On the basis of present studies it is possible to make up a general scheme of the genesis of the alkali soils for this section of the Great Plains. Such a scheme is shown in figure 5.

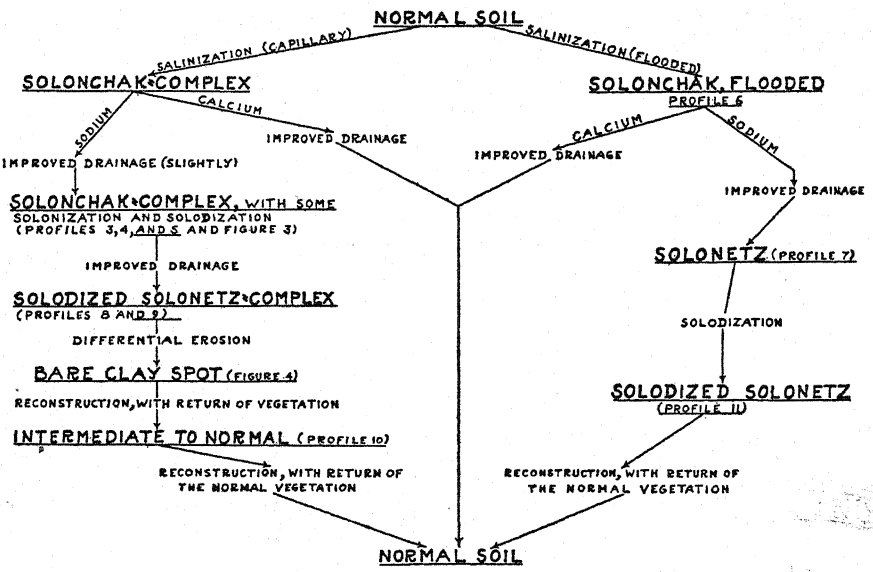


FIG. 5. AN OUTLINE OF THE CYCLE OF EVOLUTION OF THE ALKALI SOILS IN WESTERN NORTH DAKOTA

Importance of Vegetation

The vegetation on the soils of the solonchak and solonetz-complex consists of grasses or grass-like plants. That the character of the plants varies widely is well known. As a matter of fact the ash content and the relative percentages of different compounds in the ash vary more widely between various species of the semi-arid regions than do the characters between most timber types.

Nearly all data on mature profiles undergoing leaching show a concentration of bases in the A_1 horizon. In the case of salt-loving plants growing on sodium-solonchak, a large percentage of these bases are sodium and potassium. In the case of a solodized solonetz the A_1 horizon contains a large percentage of HCl-soluble sodium and, as shown in table 6, in a rather well-advanced

solodized solonetz the amount is considerably greater than in the primary leached horizon. Thus it can be seen that the sodium goes through the solum again and again; it is leached down and returned again to the surface. As with the bases in the case of a podzol there is a gradual loss of sodium to the ground water. As the process goes on halophytic vegetation is displaced by mesophytic plants using less sodium and more calcium. Slowly, as the development continues, sodium is replaced by hydrogen and calcium in the exchange and, finally, in the return to the normal soil, calcium (with magnesium) predominates. The rôle of the vegetation in the genesis of these soils can hardly be overemphasized.

TABLE 7

pH and −d F·P of solodized solonetz (profile 11)

HORIZON	DEPTH	−d F·P	pH
	inches	°C.	
A_1	0–⅜	0.017	5.7
A_2	⅜–4½	0.007	5.85
A_{21}	4½–9	0.018	5.85
B_2	9–15	0.023	7.35
B_3	15–23	0.037	8.15
C_1	23–30	0.048	8.45
C	30+	0.112	7.55

TABLE 8

Exchange material extracted from solodized solonetz, profile 11 by treatment with 0.05 N HCl*

(M.e. per 100 gm. soil)

HORIZON	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TOTAL	C_2O	NET
	inches											
A_1	0–⅜	5.86	21.55	4.51	3.94	19.87	8.70	0.90	1.51	66.93		66.93
A_2	⅜–4½	7.31	24.90	3.75	1.22	9.41	5.80	0.64	1.90	55.93		55.93
A_{21}	4½–9	8.40	27.88	5.10	0.48	7.31	9.25	0.34	1.70	60.46		60.46
B_2	9–15	8.35	25.29	3.82	0.56	12.06	12.67	0.54	3.78	67.19		67.19
B_3	15–23	14.58	23.58	3.90	1.76	16.20	21.42	0.59	4.75	86.78		86.78
C_1	23–30	19.24	52.67	12.02	1.13	50.71	14.25	0.88	4.31	155.21	50.90	104.31
C	30+	17.24	44.46	13.60	1.08	64.18	17.79	0.83	3.91	163.09	46.80	116.29

* Analyses by G. J. Hough.

Micro-Relief

One of the greatest points of interest in these soils, especially from a practical point of view, is the development of a pronounced micro-relief due to the differential erosin of the eluviated horizon of the solodized solonetz-complex. These spots do not appear in the solonetz soils developed from the more nearly

uniform solonchak of the flooded type, but as such uniformity is uncommon, nearly all of the solonetz is of the complex type and subject to differential erosion. The somewhat higher rims around these spots suggest that some considerable part of the erosion is carried on by wind action. The presence of small drainage channels from nearly every spot also suggests the influence of water.

Such a typical eroded spot as that shown in figure 4 is largely barren of vegetation. As a consequence, the grazing value of land having many of these spots is greatly reduced. As from 10 to 60 per cent of the land surface in many areas of otherwise good soil is occupied by such spots the importance of this feature is apparent. When these areas are plowed the soil in the spots is so poor in physical condition that plants make little or no growth. If care is taken to use manure on the barren areas, continued tillage tends to leaven them somewhat. But, in general, farmers are not inclined to break new land in such condition at present.

SUMMARY

The morphology of the solonchak and solonetz soils of western North Dakota were studied in order to understand their classification and genesis. It was found that normal soil, solonchak, solonetz, and soloth do not represent exclusive categories, either of morphology or of genesis. Such a soil as the solonchak-complex may show some characteristics of both solonetz and soloth; and nearly every solonetz shows some properties of solonchak or soloth.

The general cycle of the genesis of these soils from the normal soil, and back again to the normal soil, both for the complex types and the flooded types, is shown.

The great importance of the different kinds of vegetation in the evolution of these soils is emphasized.

Special attention is directed to the profiles of the solodized solonetz-complex. The differential erosion of the eluviated horizons of such soils gives rise to a pronounced micro-relief, greatly lowering the value of the land for either native or cultivated plants.

REFERENCES

(1) Bouyoucos, G. J. 1927 The hydrometer as a new and rapid method for determining the colloidal content of soils. *Soil Sci.* 23: 319–330.

(2) Bouyoucos, G. J., and McCool, M. M. 1915 The freezing point method as a new means of measuring the concentration of the soil solution in the soil. Mich. Agr. Exp. Sta. Tech. Bul. 24.

(3) Gedroiz, K. K. 1925 Soil absorbing complex and the absorbed soil cations as a basis of genetic soil classification. Nosovka Agr. Exp. Sta. Pub. 38. (Translation into English from the Russian by S. A. Waksman.)

(4) Kelley, W. P. 1922 Variability of alkali soil. *Soil Sci.* 14: 177–189.

(5) Kellogg, Charles E. 1930 Preliminary study of the profiles of the principal soil types of Wisconsin. Wis. Geol. and Nat. Hist. Survey Bul. 77A.

(6) Shutt, Frank T., and Macoun, John M. 1923 On the nature of burn-outs. *Proc. and Trans. Roy Soc. Canada.* (Third Ser.) 17: (sec. 3) 79–82.

(7) VILENSKY, D. G. 1932 Brief history and principal summary of saline and alkali soils in U. S. S. R. *Proc. Second. Internatl. Cong. Soil Sci.* (Leningrad, 1930) 5: 309–326.

(8) WILLIS, E. A., ROBESON, F. A., AND JOHNSTON, C. M. 1931 Graphical solution of the data furnished by the hydrometer method of analysis. *Pub. Roads* 12: 208–215.

(9) WINTERMYER, A. M. 1931 Procedure for treating soils for the determination of subgrade soil constants. *Pub. Roads* 12: 197–207.

PLATE 1

FIG. 1. A typical view of the solonchak-complex.

FIG. 2. A typical view of the solodized solonetz-complex.

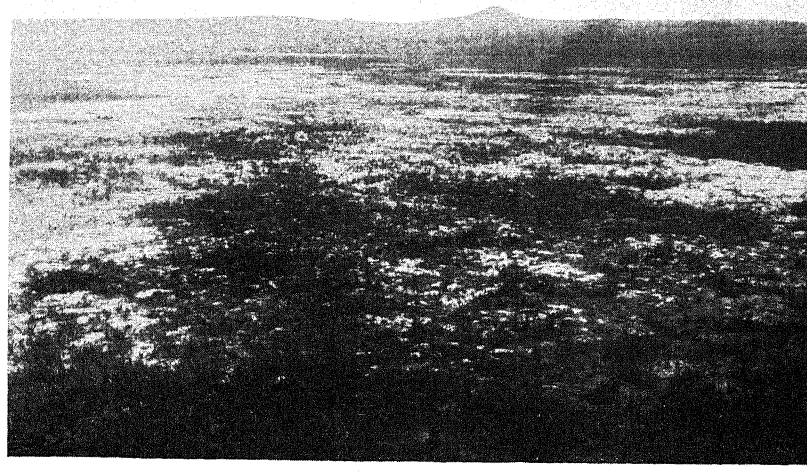


FIG. 1

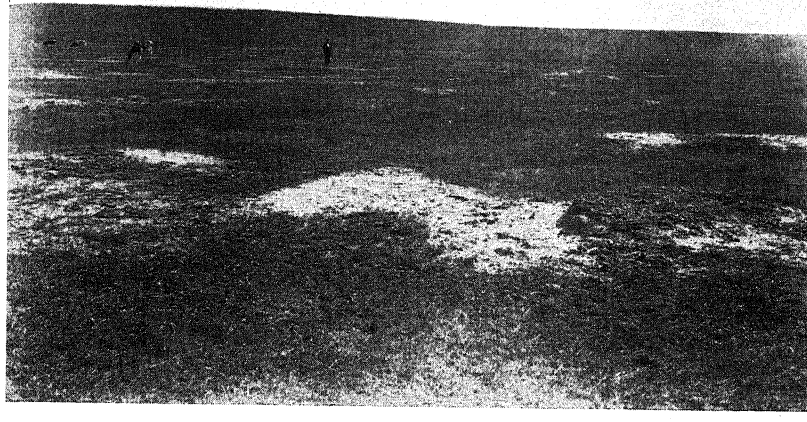
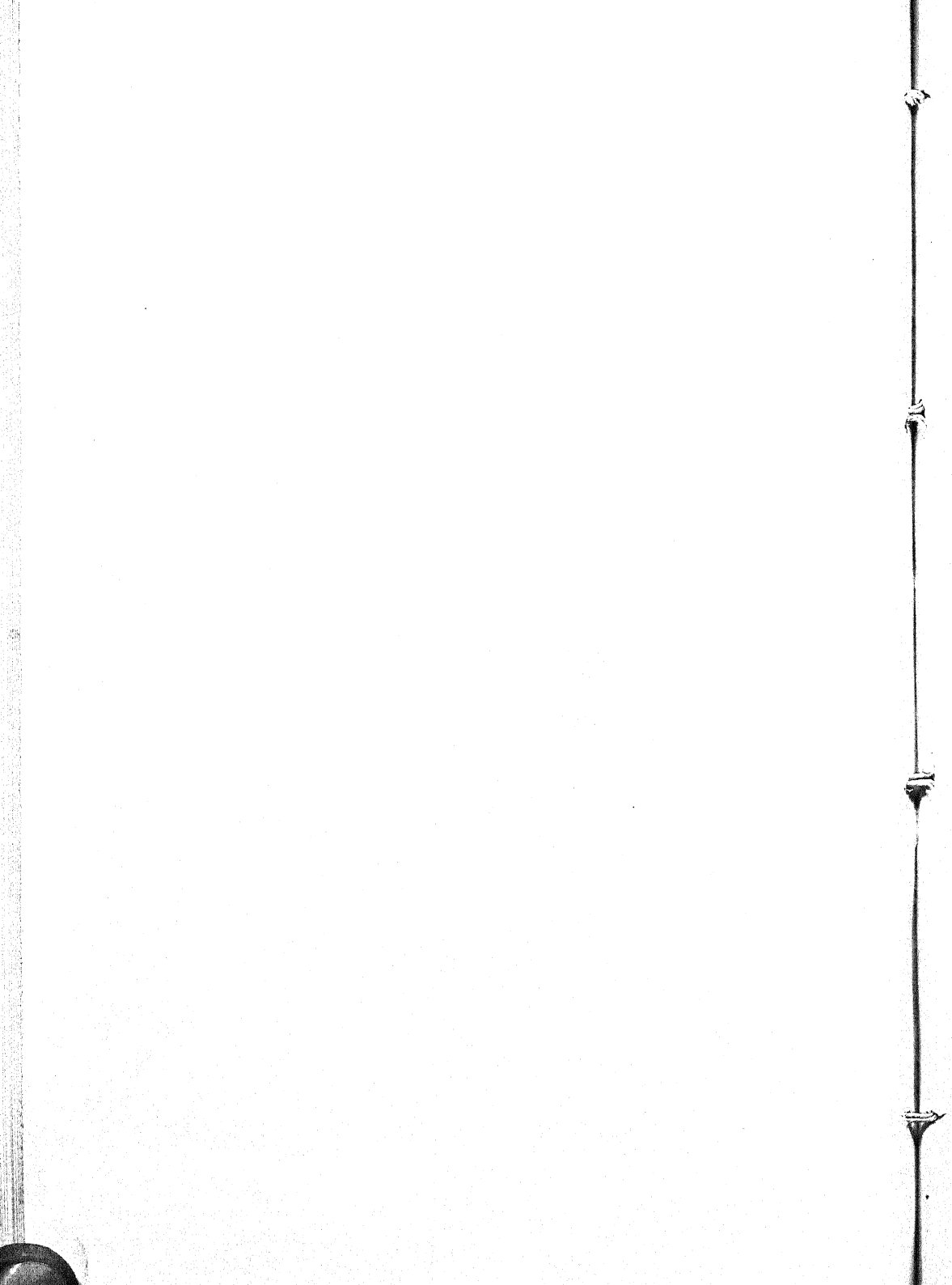


FIG. 2

LIBRARY.



LIBRARY.

AUTHOR INDEX

Abramson, H. A. Electrokinetic Phenomena and Their Application to Biology and Medicine (book review), 420.

Affleck, C. Application of the theory of probability to the size distribution of soil aggregates, 113–119.

Anderson, D. A. *See* **Walker, R. H.,** and Brown, P. E.

Anderson, M. S., and Byers, H. G. Carbon-nitrogen ratio in relation to soil classification, 121–138.

Baver, L. D. *See* **Winterkorn, H.**

Bennett, H. Practical Everyday Chemistry (book review), 423.

Bodenheimer, F. S., and Reich, K. Studies on soil protozoa, 259–265.

Bodman, G. B., and Edlefsen, N. E. Soil-moisture system, 425–444.

Boguslawski, E. von. Eilhard Alfred Mitscherlich—To the sixtieth birthday of the German investigator, 83–85.

Bouyoucos, G. J. Comparison between the pipette method and the hydrometer method for making mechanical analyses of soil, 335–345; method for determining the degree of decomposition that unknown decayed vegetable organic materials have already undergone in nature, 477–482.

Brown, P. E. *See* **Walker, R. H.,** Anderson, D. A., and.

Byers, H. G. *See* **Anderson, M. S.**

Chadwick, L. C. *See* **Laurie, A.**

Collings, G. H. Commercial Fertilizers. Their Sources and Use (book review), 418.

Corbet, A. S. Studies on tropical soil microbiology: II. The bacterial numbers in the soil of the Malay Peninsula, 407–416.

Cunningham, A. Practical Bacteriology (book review), 423.

Dhar, N. R. *See* **Tandon, S. P.**

Dowell, A. A., and Jesness, O. B. American Farmer and the Export Market (book review), 421.

Edlefsen, N. E. New method of measuring the aqueous vapor pressure of soils, 29–35; *see* **Bodman, G. B.**

Emmert, E. M. Rapid method for the determination of total nitrogen in soil, 139–142.

Farris, N. F. Root habits of certain crop plants as observed in the humid soils of New Jersey, 87–111.

Fieger, E. A., and Sturgis, M. B. Profile studies of the Coastal Prairie soils of Louisiana: I. Exchange and solution properties, 267–277.

Fowells, H. A., and Stephenson, R. E. Effect of burring on forest soils, 175–181.

Fred, E. B. *See* **Mehlich, A.,** and Truog, E.

Fresenius, L. *See* **Lemmermann, O.**

Godfrey, G. H. Indicator plants for measuring soil populations of the root-knot nematode, *Heterodera marioni* (Cornu) Goodey, 3–27.

Gopala Rao, G. Newer aspects of nitrification: I., 143–159.

Greaves, J. E. Arsenic content of soils, 355–362.

Heck, A. F. Effect of the degree of base saturation of a soil on its capacity to fix phosphorus in difficultly available form, 463–470.

Henrici, A. T. Biology of Bacteria. An Introduction to General Microbiology (book review), 418.

Jenny, H., and Leonard, C. D. Functional relationships between soil properties and rainfall, 363–381.

Jesness, O. B. *See* **Dowell, A. A.**

Joffe, J. S., and Kardos, L. T. Note on the determination of titanium in soils, 241–243.

Joffe, J. S., and Pugh, A. J. Soil profile studies: VI. Distribution of titanium in soils with special reference to podzols, 245–257.

Kardos, L. T. *See* **Joffe, J. S.**

Kellogg, C. E. Morphology and genesis of the solonetz soils of western North Dakota, 483–501.

Laurie, A., and Chadwick, L. C. Commercial Flower Forcing (book review), 417.

Lemmermann, O., and Fresenius, L. Methoden für die Untersuchung des Bodens (book review), 419.

Leonard, C. D. *See* **Jenny, H.**

McGeorge, W. T. Determination of phosphate availability in calcareous soils by electrodialysis, 347–353.

Mattson, S., and Pugh, A. J. Laws of soil colloidal behavior: XIV. The electrokinetics of hydrous oxides and their ionic exchange, 299–313.

Mehlich, A., Fred, E. B., and Truog, E. Cunninghamella plaque method of measuring available phosphorus in soil, 445–461.

Merkle, F. G. Base exchange studies on the Pennsylvania Jordan field plots, 37–64.

Paulie, E. Microflora of Kazakstan sands (central Asia), 401–406.

Pugh, A. J. Laws of soil colloidal behavior: II. Ionic exchange with hydroxides, 161–173; III. Colloidal phosphates, 315–334; *see* **Joffe, J. S.; Mattson, S.**

Ravikovitch, S. Anion exchange: I. Adsorption of the phosphoric acid ions by soils, 219–239; II. Liberation of the phosphoric acid ions adsorbed by soils, 279–290.

Reich, K. *See* **Bodenheimer, F. S.**

Scholz, H. F. *See* **Wilde, S. A.**

Shoemaker, J. S. Small-Fruit Culture (book review), 417.

Snider, H. J. Solubility of phosphorus in soils from some Illinois experiment fields, 471–476.

Spencer, V. E., and Stewart, R. Phosphate studies: I. Soil penetration of some organic and inorganic phosphates, 65–79.

Stephenson, R. E. *See* **Fowells, H. A.**

Stewart, R. *See* **Spencer, V. E.**

Sturgis, M. B. *See* **Fieger, E. A.**

Tandon, S. P., and Dhar, N. R. Influence of temperature on bacterial nitrification in tropical countries, 183–189.

Truog, E. *See* **Mehlich, A.**, Fred, E. B., and.

Vandecaveye, S. C., and Villanueva, B. R. Microbial activities in soil: I. Nitrogen fixation by Azotobacter and activity of various groups of microbes in Palouse silt loam, 191–205.

Villanueva, B. R. *See* **Vandecaveye, S. C.**

Walker, R. H., Anderson, D. A., and Brown, P. E. Physiological studies of Rhizobium: II. The effect of nitrogen source on oxygen consumption by *Rh. meliloti*, *Rh. trifolii*, and *Rh. phaseoli*, 207–217.

Wilde, S. A., and Scholz, H. F. Subdivision of the Upper Peninsula experimental forest on the basis of soils and vegetation, 383–399.

Willcox, O. W. Reshaping Agriculture (book review), 422.

Winterkorn, H., and Baver, L. D. Sorption of liquids by soil colloids: I. Liquid intake and swelling by soil colloidal materials, 291–298.

Wright, C. H. Soil Analysis. A Handbook of Physical and Chemical Methods (book review), 421.

SUBJECT INDEX

Adsorption—
anion, 163, 308.
cation, 304.
solubility and, 166.
Agriculture, Reshaping (book review), 422.
Alkaline, physiologically, salts, effect on phosphate liberation, 289.
American Farmer and the Export Market (book review), 421.
Ammonia—
exchangeable, 42–56.
oxidation of—
as affected by catalysts, 147.
photochemically, 144.
Anion—
adsorption, 308.
exchange in soils, 219–239, 279–290.
Arsenic content of soils, 355.
Azotobacter, nitrogen fixation by, 191.
Bacteria—*see* also Microbes.
Biology of (book review), 418.
numbers in tropical soil, 407.
Rhizobium, oxygen consumption by, 207.
Bacteriology, Practical (book review), 423.
Base—
exchange—*see* also Cation
of hydroxides, 172.
properties of coastal prairie soils, 267.
studies on the Pennsylvania field plots, 37–64.
exchange, as affected by—
ammonium sulfate, 51.
dried blood, 49.
lime, 44, 54.
manure, 43.
nitrate of soda, 50.
nitrogen carriers, 56.
potash, 46, 54.
salt water, 274.
superphosphate, 46, 47.
saturation—
effect on phosphorus fixation, 463.
method of determining, 38.
saturation, as affected by—
ammonium sulfate, 51.
cropping, 42.
dried blood, 49.
lime, 44, 54.
manure, 43.
nitrate of soda, 50.
nitrogen carriers, 56.
potash, 46, 54.
superphosphate, 46, 47.
saturation, relation to—
hydrogen-ion concentration, 464.
rainfall, 375.
Bases—
exchangeable—
effect of treatments on, 37.
in virgin and irrigated mounds, 273.
method of determining, 40.
nitrification effects on solubility of, 178.
Braunerde, titanium in, 255.
Calcium—*see* also Lime.
exchangeable, 42–56.
exchangeable, relation to phosphorus fixation, 465.
glucose phosphate, penetration of, into the soil, 76.
glycerophosphate, penetration of, into the soil, 76.
glycol phosphate, penetration of, into the soil, 76.
hydroxide, effect on phosphate release from soils, 280.
saturated soil, phosphorus pentoxide absorption by, 225.
sorbityl phosphate, penetration of, into the soil, 76.
Capillarity, *see* Moisture, capillary.
Carbon-nitrogen ratio in major soil groups of the U. S. A., 121–138.
Cation—
adsorption, 304.
exchange as affected by—
calcium hydroxide, 280.
sodium hydroxide, 285.
Chemistry, Practical Everyday (book review), 423.
Chernozem—
carbon in profile of, 124.

Chernozem—(*continued*)
carbon-nitrogen ratio—
colloids of, 125.
soils, 124.
nitrogen in profile of, 124.
Climate, location of boundary between arid and humid, 379.
Clover, red, root development of, in humid soils, 99.
Colloids—
inorganic, amount of, as affected by rainfall, 371.
isoelectric point and ion exchange in, 162.
laws governing behavior of soil, 161, 299.
silica-sesquioxide ratio of, as a function of water intake, 296.
soil, sorption of liquids by, 291–298.
Corn, root development of, as affected by soil conditions, 103.
Cunninghamella plaque method for available phosphorus in soil, 445–461.
Daikuhara, Gintaro, obituary note on, 1.
Electrodialysis, phosphate availability as determined by the method of, 347–353.
Electrokinetic Phenomena and their Application to Biology and Medicine (book review), 420.
Fertilizers, Commercial (book review), 418.
Flower Forcing (book review), 417.
Forests, subdivision of, on basis of soils and vegetation, 383–399.
Fruit, Small-, Culture (book review), 417.
Humus, in burnt forest soils, 180.
Hydrogen—
exchangeable, 42–56.
exchangeable, relation to rainfall, 373.
saturated soils, adsorption of phosphorus pentoxide by, 220.
Hydrogen-ion concentration—
effect on—
microbial activity in soils, 201.
phosphoric acid adsorption by the soil complex, 230.
relation to—
ammonium sulfate, 51.
cropping, 42.
degree of saturation, 56.
dried blood, 49.
isoelectric precipitation of hydroxides, 301.
lime, 44, 54.
manure, 43.
nitrate of soda, 50.
nitrogen carriers, 56.
potash, 46, 54.
rainfall, 373.
superphosphate, 46, 47.
Hydroxides—
electrokinetics of, 299.
ionic exchange with, 161, 299.
Isoelectric—
point of a series of hydroxides, 300.
precipitation in the titanium-hydroxide system, 250.
Laterite soils, 132.
Lateritic soils—
carbon in profile of, 131.
carbon-nitrogen ratio in, 131.
genetic relation of, to podzolic soils, 250.
nitrogen in profile of, 131.
Lime, effect on—
liberation of phosphate, 289
nitrogen fixation, 194.
Magnesium, exchangeable, 42–56.
Manure, effect on nitrogen fixation, 194.
Microbes—*see* also Bacteria.
groups of, activity in soil, 191.
in Kazakstan sands, 401.
reaction effects on soil, 201.
Mitscherlich, E. A., to his sixtieth birthday, 83.
Mitscherlich method for phosphorus availability as compared with other methods, 457.
Moisture—
capillary potential of, relation to vapor pressure, 435.
mechanical forces, action on soil, 429.
movement in soil, 438.
soil system, 425.
Nematodes, root-knot in soils, 3.
Nitrates—
distribution of, at different depths, 154.
non-biological, formation of, 158.
Nitrification—
bacterial—
in tropics, 183–189.
versus chemical, 151.
calcium versus magnesium carbonate, effect on, 186.
chemical, 144, 187.
newer aspects of, 143–159.
studies in forest soils, 176.
Nitrite—
formation of, photochemically, 148.
oxidation of, to nitrates, 158.
Nitrogen—
fixation in soils, 191.

in—
chernozem, 124.
lateritic soils, 131.
podzolic soils, 129.
podzols, 128.
prairie soils, 126.
method of determining, in soils, 139–142.
nitric—
relation to radiant energy of sun, 156.
seasonal variation of, in atmosphere, 155.
organic and inorganic, photochemical oxidation, 152.
rainfall function relationships, 368.
Organic matter, degree of decomposition, method of determining, 477–482.
Phosphates—
availability of, 66.
availability of, as determined by electrodialysis, 347.
colloidal, study of, 315.
effect on base exchange, 46.
root zone distribution of, 69.
soil penetration of organic and inorganic, 65–79.
structure of, 316.
Phosphoric acid—
adsorption by soils, 219.
liberation of adsorbed, in soils, 279.
Phosphorus—
available, in soil, 445.
fixation of, 463.
solubility of, in soils, 471–476.
Plants, indicator for measuring population of nematodes in soils, 3.
Podzol—
analyses of, soils, 254.
carbon content of the, profile, 128.
carbon-nitrogen ratio of, 128.
nitrogen content of the, profile, 128.
soils, 387.
swampy, soils, 388.
titanium content of the, profile, 245.
Podzolic soils—
gray-brown—
carbon in profile of, 129–130.
carbon-nitrogen ratio, 129–130.
nitrogen in profile of, 129–130.
yellow and red—
carbon in profile of, 129–130.
carbon-nitrogen ratio, 129–130.
nitrogen in profile of, 129–130.
titanium in, 255.
Potassium, exchangeable, 42–56.
Potatoes—
root development of, in humid soils, 89.
yield of, as affected by spacing and seed piece, 98.
Prairie—
carbon-nitrogen ratio of, soils, 126.
coastal, soils, profile studies, 267–277.
Protozoa, soil, studies on, 259–265.
Rainfall, relation to soil properties, 363–381.
Red soils, titanium in, 255.
Rhizobium, *see* Bacteria.
Root—
clover (red), as affected by soil conditions, 99.
corn, as affected by soil conditions, 103.
habits of certain crop plants in soils of New Jersey, 87–111.
potato, as affected by—
fertilizers, 93.
seed piece, 94.
zone, distribution of nutrients within the, 69.
Silica-sesquioxide ratio, water intake as a function of, 296.
Sodium—
exchangeable, 42–56.
hydroxide, effect on exchangeable cations and anions, 285.
Soil—
acidity, relation to rainfall, 373.
aggregates, size distribution of, 113–119.
Analysis (book review), 421.
calcium saturated soil, 225.
classification, relation to carbon : nitrogen ratio, 121–138.
colloidal behavior, laws of, 161, 299, 315.
colloids, *see* Colloids.
formation, intensity of, 377.
hydrogen saturated, 221.
mechanical analysis of, comparison of methods, 335–345.
Methods of Investigation (book review), 419.
microbial activities in, 191–205.
moisture, *see* Moisture.
moisture system, 425–444.
Pennsylvania, fertility plots, studies on, 37.
phosphates—*see* also Phosphates, Phosphorus.
organic and inorganic, penetration of, 65.
release of adsorbed, 279.

Soil—(*continued*)
plots, Pennsylvania fertility, 37–64.
profile—
chernozem, 124.
lateritic, 131.
podzol, 128.
podzolic, 129.
prairie, 126, 267.
studies, 245–257, 267.
properties, relation to rainfall, 363.
protozoa, 259; *see* also Protozoa.
reaction, effect on microbial activity, 201.
root-knot nematode population in the, 3–27.
solonetz, *see* Solonetz.
sterilized, effect on ammonia oxidation, 152.
tropical, microbiology of, 407–416.
water table, disappearance of, 437.
Soils—
anion exchange in, 219.
arsenic content of, 355–362.
base saturation in, 38, 220.
Braunerde, *see* Braunerde.
calcareous, phosphate availability, 347.
chernozem, *see* Chernozem.
forest—
effect of burning on, 175–181.
management and, 391.
subdivision on basis of, 383.
gray-brown podzolic, *see* Podzolic soils.
humid, of New Jersey, root penetration as observed in, 87.
hydrogen-ion concentration, *see* Hydrogen-ion concentration.
hydrogen saturated, 221.
laterite, *see* Laterite.
lateritic, *see* Lateritic.
manured, effect on nitrogen fixation, 194.
muck, 389.
nitrogen in, *see* Nitrogen.
Palouse silt loam, microbial activities in, 191.
phosphoric acid liberation in, 279.
podzol, 387; *see* also Podzol, Podzolic soils.
prairie, *see* Prairie.
red and yellow podzolic, *see* Podzolic soils.
sandy, of Kazakstan, flora of, 401–406.
titanium determination in, 241.
unsaturated, 221.
vapor pressure of, method of measuring, 29–35.
yellow and red, titanium in, 255.
Solonchak, profile study of, 489.
Solonetz—
morphology and genesis of, 483–501.
solonchak stage leading to, 489.
Titanium—
determination of, in soils, 241–243.
distribution of—
in colloid fraction of various soils, 255.
in soils, 245.
effect on oxidation of ammonia, 148.
Unsaturation, effect on phosphate adsorption by the soil complex, 230.
Urea, oxidation of, photochemically, 152.
Vapor pressure—
curves of sand and clay, 427.
of soils, 29.
Vegetation—
as basis for subdividing forests, 383.
importance of, in saline soils, 497.
Water table, *see* Soil water table.
Yellow soils, titanium in, 255.